FORMATION OF BONDS TO CARBON AT TRANSITION METAL CENTERS

thesis by

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To Boogh

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Abstract

The reactions of $Cp_2\overline{TiCH_2Al(Me)_2}Cl$ 1, $Cp_2\overline{TiCH_2C(R)=CR}$ 2, and $Cp_2\overline{TiCH_2CHRCH_2}$ 3 with organic carbonyl compounds are explored. 1 with carbonyl, in a Wittig-type reaction, exchanges methylene for oxygen and yields alkenes; no intermediates can be observed. When treated with carbonyl, 2a (R=Ø) inserts O=C into the Ti-CH_2 bond, generating oxytitanacyclohexenes. Other metallacyclobutenes similarly insert carbonyl; or, if RC≡CR is labile, exchange methylene for oxygen, producing alkenes. 3a (R=t-butyl) with carbonyl compounds also exchanges methylene for oxygen, and the mechanism of this reaction is explored. 3a is in equilibrium with a titanocene-carbene-olefin complex 11, which is trapped by ketones. 11 is also in equilibrium with titanocene carbene 12 and free olefin; 12 is trapped by esters (as well as ketones). The formation of 11 is rate-determining. Formation of 12 from 11, trapping of 11 by ketone, and the reverse reaction, formation of 3a from 11 are all competitive. Trapping of 12 by esters is competitive with the reverse reaction, formation of 11 from 12 and olefin. Relative rates of reaction of several ketones and esters are determined.

A new platinum vinyl complex, $L_2Pt(CH=CH_2)Me$ 3 ($L=PMe_2Ø$) is prepared by treatment of the known $L_2Pt(CH=CH_2)Cl$ with MeLi at low temperatures. Oxidative addition of MeI to the platinum (II) complex 3 generates $L_2Pt(CH=CH_2)Me_2I$ 4. The thermal

decomposition of 4 is examined, and the relative amounts of ethane and propene formed lead to the conclusion that a vinyl group reductively eliminates twenty times faster than methyl.

$CpCr(NO)_2Me$ is treated with various ligands in an attempt to see insertion of NO into the Cr-Me bond. A clean reaction is observed with PMe_3. Instead of insertion, deoxygenation of NO by PMe_3 generates $O{=}PMe_3$ and, ultimately, $CpCr(NO)(:NMe)(PMe_3)$ 5a. Similar reactions occur with $CpCr(NO)_2R$, R=n-hexyl, isobutyl, Ø, Thermal decomposition of 5a or treatment with H^+ generates CH_4.

Abbreviations

Bu = butyl, $-C_4H_9$

Cp = $(\eta^5-C_5H_5)$, cyclopentadienyl

Cp* = $(\eta^5-C_5(CH_3)_5)$, pentamethylcyclopentadienyl

diphos = bis-1,2-(diphenylphosphino)ethane

Et = ethyl, $-C_2H_5$

L = ligand, generally a phosphine or CO

M = transition metal

Ø = phenyl, $-C_6H_5$

R = alkyl

THF = tetrahydrofuran

Table of Contents

Table of Contents, Continued

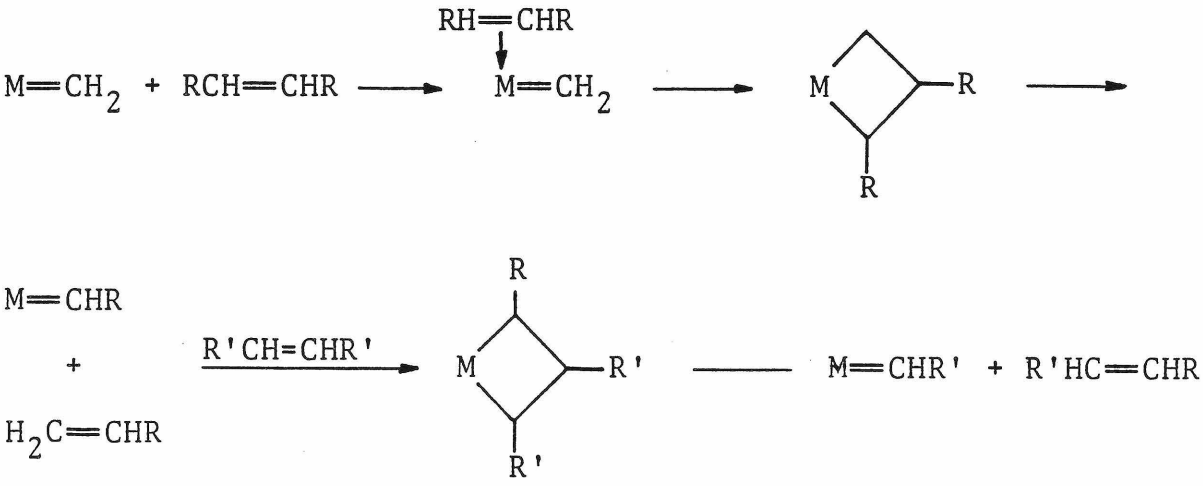
CHAPTER I

REACTIONS OF TITANACYCLOBUTANES AND -BUTENES WITH HETEROATOM-CARBON DOUBLE BONDS

Introduction

Interest in metallacyclobutanes, particularly as intermediates in olefin metathesis (Scheme I) has a long history.[1] The currently accepted mechanism requires a transition metal carbene, the origin of which is not

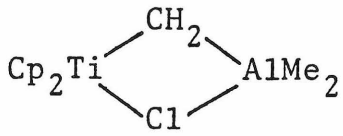
Scheme I



M = transition metal

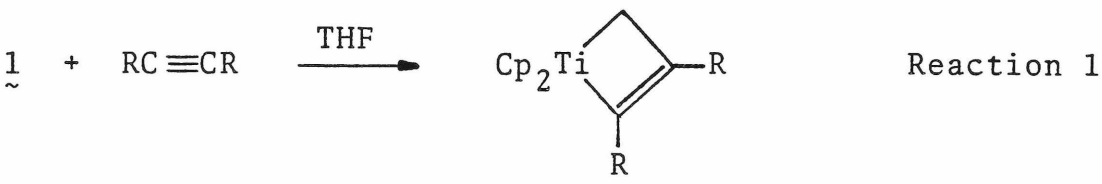
always clear. Many metathesis catalyst systems contain a low-valent transition metal (frequently Mo or W) and a good Lewis acid (such as $AlMe_3$), and may be homogeneous or heterogeneous. An important clue to the role of the co-catalyst is found in the methylene-bridged titanium

aluminum complex 1, isolated by Tebbe and Parshall from the reaction between Cp_2TiCl_2 (Cp = η^5-cyclopentadienyl) and $AlMe_3$,[2] the same product can be obtained from Cp_2TiMe_2 and Me_2AlCl.



1

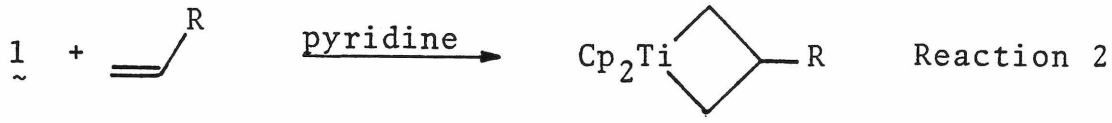
Not only does 1 metathesize olefins,[3] but it does so more rapidly in the presence of a good Lewis base (e.g., THF).[4] Tebbe succeeded in isolating metallacyclobutenes 2 from the reaction of 1 and an acetylene in THF solution (Reaction 1).[4]



Reaction 1

2a, R = ϕ
b, R = $SiMe_3$

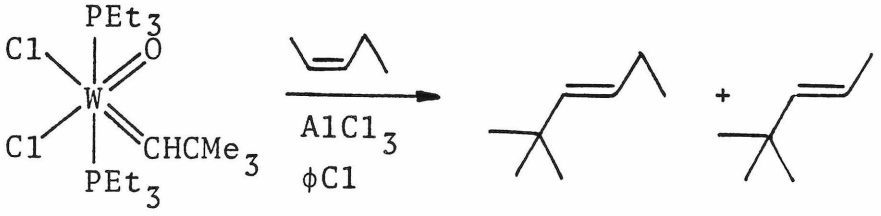
Recently, metallacyclobutanes 3 have been isolated from this system, using pyridine as Lewis base (Reaction 2).[5] Work in our laboratories is continuing to elucidate the nature of the interaction between Me_2AlCl and 3.



Reaction 2

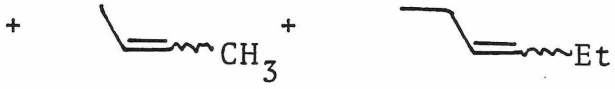
3a, R = t-butyl
b, R = i-propyl

Schrock[6] has isolated a tungsten carbene 4 which, in the presence of $AlCl_3$, metathesizes olefins for many turnovers (Reaction 3).

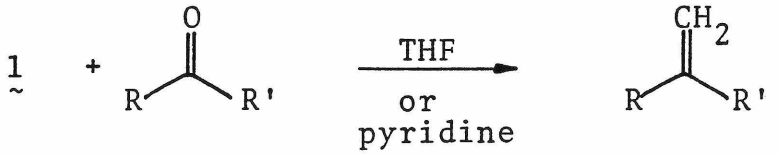


Reaction 3

4



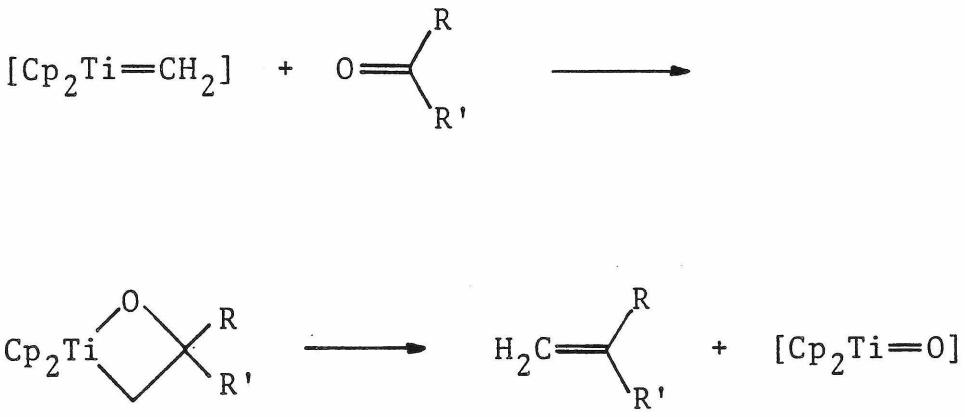
Tebbe has also reported that 1, with organic carbonyl compounds, in a Wittig-type reaction, will exchange methylene for oxygen,[2] and Pine et al[7] demonstrated that this is a general reaction, again promoted by the presence of a Lewis base (Reaction 4). It is tempting to consider that a mechanism similar to that suggested for olefin



Reaction 4

metathesis is operating (Scheme II), and this led us to investigate the reactions between 1, 2, and 3 and carbonyl compounds.

Scheme II



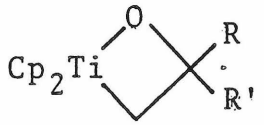
Results and Discussion

I. Reactions of 1 With Heteroatom-Carbon Double Bonds. It has been reported[2,7] that the reaction of 1 with organic carbonyl compounds produces Wittig-type alkene products in good yields. The organometallic product, which is formed more slowly than the alkene, is $Cp_2Ti(Me)Cl$.[8]

We have found that a similar reaction is observed when a C=N (instead of C=O) bond is present (Reaction 5), but in poorer (up to 38%) yields.

$$1 + \phi CH{=}NMe \longrightarrow \phi CH{=}CH_2 \qquad \text{Reaction 5}$$

Our attempts to observe intermediate organometallic products (such as 5) were unsuccessful, even using pyridine as base (the best base for synthesis of metalla-



5

cyclobutanes 3[5]) and trimethylacetaldehyde as the carbonyl substrate (3a is the most stable of the metallacyclobutanes synthesized to date[5]). Even at low temperatures, one

could see no evidence for 5 in the NMR, although eventually some 3a is produced, presumably from 1 and 3,3-dimethyl-1-butene, both of which can be observed at intermediate stages of the reaction.

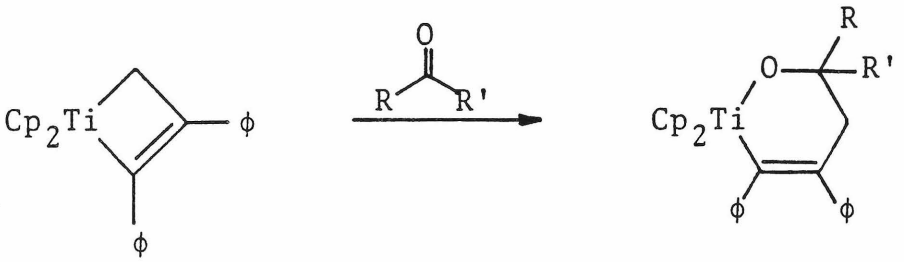
Either 5 is not an intermediate in Scheme II, or it reacts to give alkene and titanocene oxide very rapidly. The discussion of these possibilities will be delayed until the entire mechanism of the reaction between 1 and 3 and organic carbonyl compounds is considered (vide infra).

Reaction of 1 with the simplest "carbonyl" compound, CO, has previously been found to yield neopentane.[9] In our hands, the organic products varied with reaction time, but included methane, ethylene, ethane, propene, isobutylene, and other C_4 and higher hydrocarbons.[10] No ketene, allene or acetylene was observed. The only organometallic product observed is $Cp_2Ti(Me)Cl$,[11] and this is apparently unstable to the reaction mixture as it eventually disappears (although a poor yield can be isolated at early reaction times).

It is too early to speculate on the mechanism of these reactions, and while work clearly remains to be done on this system, we have instead focused on the more tractable systems described below.

II. Reactions of Titanacyclobutenes With Carbonyl Compounds. Tebbe reports that titanacyclobutene 2b has a labile bis-trimethylsilylacetylene group which can be displaced by diphenylacetylene or Me_2AlCl to yield 2a or 1, respectively. In the hope that an acetylenic group could be displaced by a carbonyl, several titanacyclobutenes were treated with a variety of carbonyl compounds.

2a reacted with a variety of carbonyl compounds to give the insertion products 6, shown in Reaction 6 and identified on the basis of their NMR and IR spectra, color, and HCl decomposition products. Reactions required approximately two days to go to completion at ambient temperatures in benzene solution; yields were quantitative by NMR.



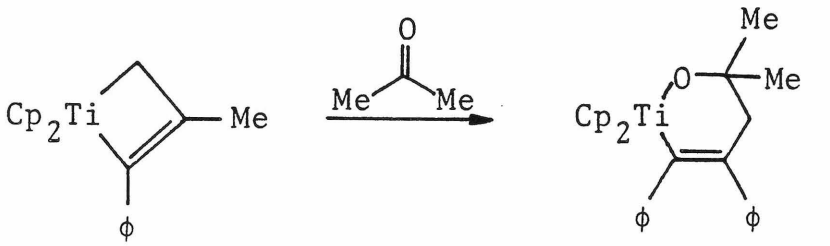
2a

6a, R=R'=Me
b, R=ϕ, R'=H
c, R=ϕ, R'=Me
d, R=t-Bu, R'=H

Reaction 6

NMR data for the various products are given in Table 1. The IR spectra showed Ti-O bands at 715 cm^{-1}, C-O stretches at 1160 cm^{-1}, and bands due to the Cp rings at 3050, 1435, 1120, 1010 and 815 cm^{-1}. C=C ring modes due to the phenyl groups appeared at 1590, 1480, and 1435. No bands appeared between 3050 and 1590 cm^{-1}.

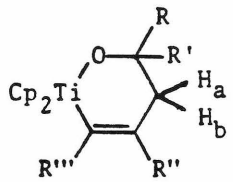
Previously unreported 2c[12] showed similar reactivity with acetone (Reaction 7); data for this complex are also included in Table 1. Reaction times for 2c were somewhat less than for 2a.



2c 6c Reaction 7

The products 6a and 6b were isolated as yellow-orange crystals. They are quite robust: they are air-stable even in solution,[14] and 6a has been heated at 170°C for weeks (in benzene-d_6 in a sealed NMR tube) without significant decomposition. The yellow-orange color and air stability are typical of other titanium alkoxide compounds.[15] Decomposition by HCl in dry ether occurs over a period of

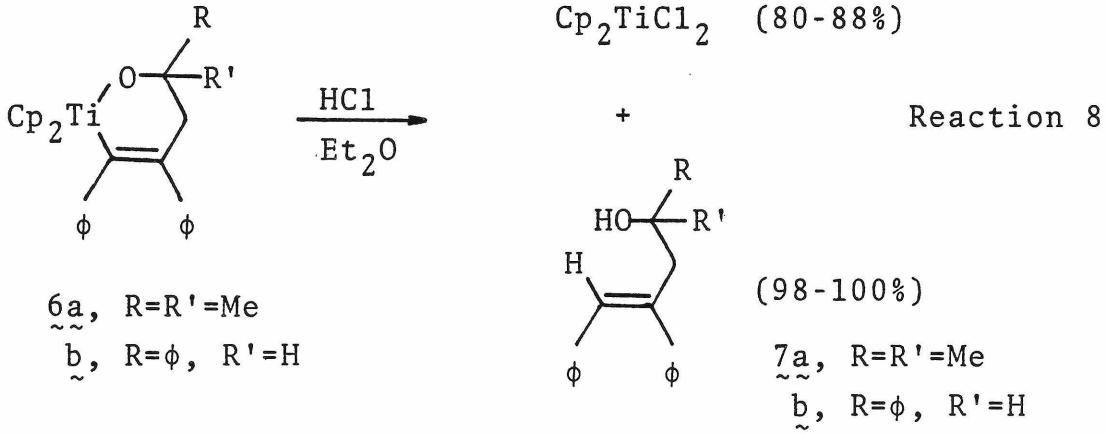
Table 1. Oxytitanacyclohexenes Obtained from the Reaction of 2 and a Carbonyl Compound.



Compound (Prepared from)	R	R'	R''	R'''	NMR in Benzene-d_6
6a (2a + acetone)	Me	Me	ϕ	ϕ	1.20 (s, 6H), R and R' 2.55 (s, 2H), methylene[a] 5.75 (s, 10H), Cp rings[b] 6.7-7.15 (m, 10H), R'' and R'''
6b (2a + benzaldehyde)	ϕ	H	ϕ	ϕ	2.85 (d, J = 4 Hz, 1H), H_a[c] 2.92 (s, 1H), H_b[c] 5.40 (m, J = 4 Hz, 1H), R'[d] 5.56 (s, 5H), Cp[e] 6.03 (s, 5H), Cp[e] 6.9-7.3 (m, 15H), ϕ groups
6c (2a + acetophenone)	ϕ	Me	ϕ	ϕ	1.55 (s, 3H), R' 2.99 (s, 1H), H_a[c] 3.03 (s, 1H), H_b[c] 5.61 (s, 5H), Cp[e] 5.97 (s, 5H), Cp[e] 6.7-7.2 (m, 15H), ϕ groups
6d (2a + trimethylacetaldehyde)	t-Bu	H	ϕ	ϕ	0.85 (s, 9H), R 2.61 (d, J = 5 Hz, 1H), H_a[c] 2.69 (s, 1H), H_b[c] 4.07 (m, J = 5 Hz, 1H), R'[d] 5.58 (s, 5H), Cp[e] 6.02 (s, 5H), Cp[e] 6.7-7.2 (m, 10H), R'' and R'''
6e (2c + acetone)	Me	Me	Me	ϕ	1.17 (s, 3H), R'' 1.54 (s, 6H), R and R' 2.30 (s, 2H), methylene[a] 5.80 (s, 10H), Cp rings[b] 6.7-7.3 (m, 5H), R'''

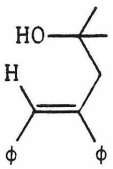
a) H_a and H_b, which are equivalent. b) Equivalent Cp rings. c) H_a or H_b, which are inequivalent. No specific stereochemical assignment with respect to R and R' is intended. d) Coupled to H_a and H_b. Actually a non-first order 4-line pattern. e) Cp rings are inequivalent. No specific assignment with respect to R and R' is intended.

approximately 15 min at room temperature, and yields the expected products, shown in Reaction 8 and identified on the basis of their NMR, IR and mass spectral data. These data is included in Table 2.



Reaction of 2a with benzaldehyde yielded a minor product (approximately 20%) as well as the major product 6b (80%). The minor product is an isomer which can occasionally be obtained nearly pure as large, dark red crystals from a toluene-pentane recrystallization of the mixture obtained from the reaction of 2a and benzaldehyde. It has been identified as isomer 8 on the basis of its NMR spectrum, color, and HCl decomposition products. These data are contained in Table 3. In particular, the deep red color is atypical of titanium alkoxide compounds, and the HCl decomposition product contains no alcoholic group, so a Ti-O bond is unlikely. Furthermore, the

Table 2. Spectral Data for the HCl Decomposition Products 7a and 7b.

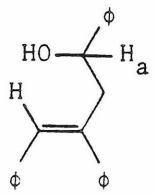


7a

NMR (CCl_4): δ 1.10 (s, 6H), Me groups
1.13 (s, 1H), -OH
2.68 (s, 2H), methylene
6.46 (s, 1H), vinyl proton[a]
6.8-7.3 (m, 10H), phenyl groups

IR (KBr): 3590 cm^{-1}, OH

MS: m/e (rel. int.)
252 (2), parent ion
234 (2), parent-H_2O[b]
219 (2), 234-CH_3
194 (100), parent-acetone
179 (43), 194-CH_3



7b

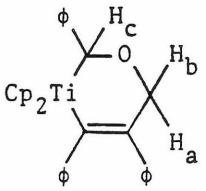
NMR (CCl_4): δ 2.04 (s, 1H), -OH
2.80 (d, J = 6.8 Hz, 2H), methylene
4.48 (t, J = 6.8 Hz, 1H), H_a
6.33 (s, 1H), vinyl proton[a]
6.8-7.3 (m, 15H), phenyl groups

IR (KBr): 3590 cm^{-1}, OH

MS: m/e (rel. int.)
300 (1), parent ion
282 (3), parent-H_2O[b]
194 (100), parent-benzaldehyde

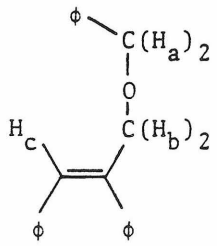
a) Compare to values of δ 6.39 for cis-methylstilbene and 6.75 for trans-methylstilbene: M. Michman and H. H. Zeiss, J. Organomet. Chem., 15, 139 (1968). HCl decomposition of 2a also yields cis-methylstilbene. b) This is a major fragment at low eV.

Table 3. Data for Oxytitanacyclohexene Isomer 8.



8

NMR (C_6D_6): δ 1.49 (s, 1H), H_a[a]
1.60 (s, 1H), H_b[a]
2.12 (s, 1H), H_c
5.62 (s, 5H), Cp[a]
6.19 (s, 5H), Cp[a]
6.7-7.2 (m, 15H), phenyl groups



Product of
HCl Decomposition

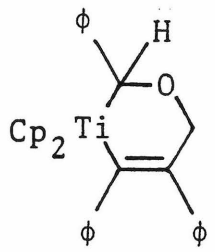
NMR (CCl_4): δ 4.95 (s, 2H), H_a
5.25 (s, 2H), H_b
6.42 (s, 1H), H_c
6.5-7.3 (m, 15H), phenyl groups

IR (CCl_4): no bands above 3200 cm^{-1}

MS: m/e (rel. int.)
300 (0.1), parent
298 (2), parent-H_2
296 (2), parent-2 H_2
282 (100), 298-O
192 (100), 298-benzaldehyde

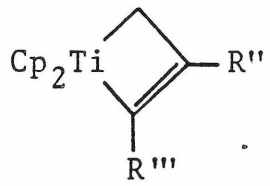
a) No specific stereochemical assignment with respect to H_c and the phenyl group on the same carbon as H_c is intended.

the vinylic proton on the HCl decomposition product is clearly seen so that the Ti-C(ϕ) bond must have remained intact and insertion must have occurred into the Ti-CH_2 bond. Compound 8 is therefore the structural assignment.



8

Compounds 2b, and the previously unreported 2d[13] and 2e,[12] reacted very slowly with carbonyl compounds. No tractable organometallic products were formed, and small amounts of alkene products from methylene for oxygen

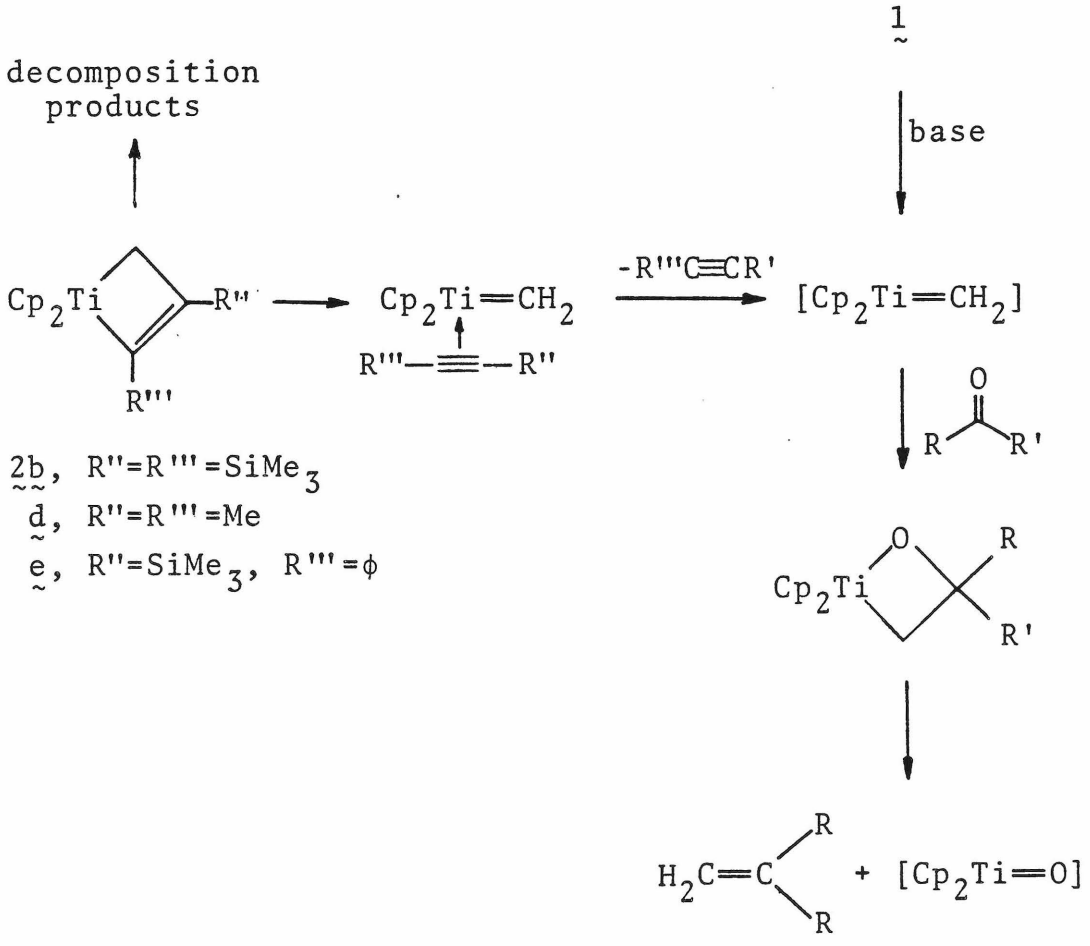


2d, R'=R'''=Me
e, R''=$SiMe_3$, R'''=ϕ

exchange (e.g., styrene from benzaldehyde) were observed. If, as Tebbe suggests,[4] 2b gives rise to the intermediate responsible for olefin metathesis (by virtue of the labile

bis-trimethylsilylacetylene) and if this intermediate is also responsible for the methylene for oxygen exchange reaction described for 1 in the presence of a Lewis base, then the alkene products are not surprising. The acetylene-carbene complex may also be responsible for some or all of the methylene for oxygen exchange. There may be, however, alternate decomposition pathways available to 2b, 2d, and 2e, accounting for the poor yields of alkene (Scheme III).

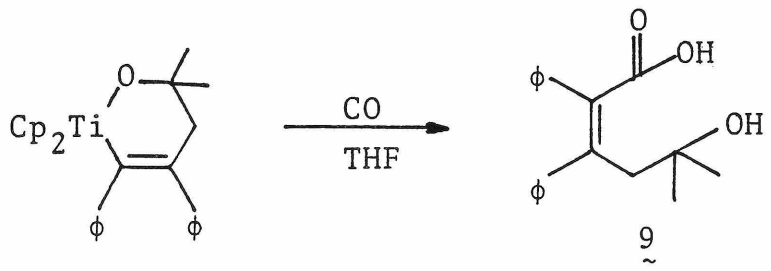
Scheme III



2b, R''=R'''=$SiMe_3$
2d, R''=R'''=Me
2e, R''=$SiMe_3$, R'''=ϕ

No reaction at all was observed between 2a and N-benzylidenemethylamine, up to temperatures sufficient to decompose 2a.

A brief study of the reactivity of 6a toward CO was conducted. Although the reaction was slow, in two weeks at 70°C in THF-d_8 in a sealed NMR tube under 1 atmosphere of CO, all 6a was observed to disappear, and a new product 9 was formed in 78% yield (by NMR) (Reaction 9). The product was identified on the basis of NMR, IR and mass



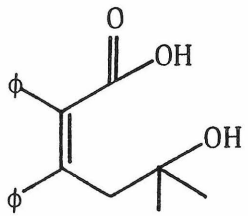
9

Reaction 9

spectral data; these are included in Table 4. While these few reactions do not establish wide generality, this does suggest a route to α,β-unsaturated acids or lactones (if an intermediate titanacycle can be made to reductively eliminate or if the product is condensed to the lactone)(Scheme IV).

While the first step, formation of the titanacyclobutene 2, has been used only once on a preparative scale,[13] it has also succeeded on a NMR-tube scale[12] and may prove to be applicable even to terminal acetylenes.[16] With the

Table 4. Spectral Data for CO Insertion Product 9.



9

NMR (THF-d_8): δ 1.10 (s, 6H), Me groups
1.20 (s, 1H), -OH
2.77 (s, 2H), methylene
6.9-7.3 (m, 10H), phenyl groups
(COOH not located)

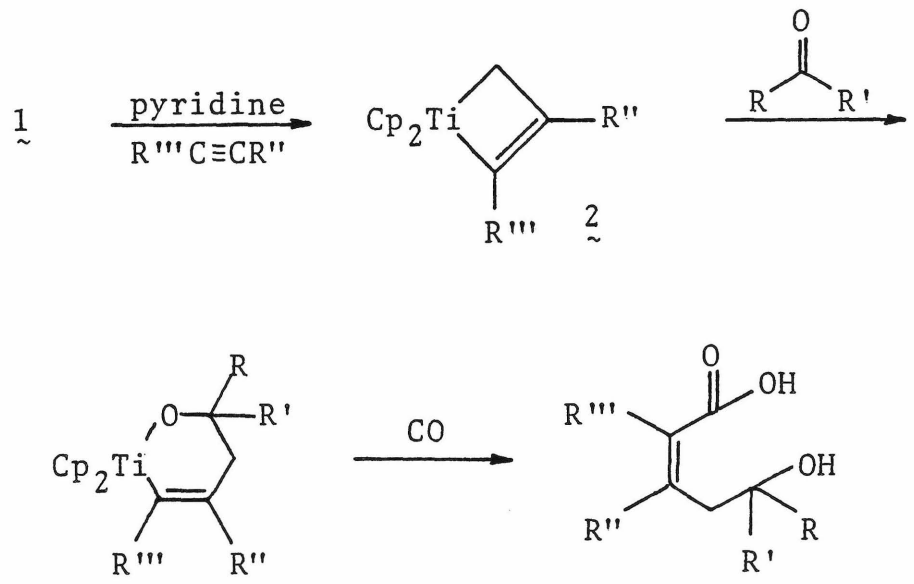
IR (CCl_4): 3450 cm^{-1} (broad, intense), -OH
1660 cm^{-1} (strong), CO stretch

MS: m/e (rel. int.)

279 (30), parent-OH[a]
178 (100), diphenylacetylene

a) Parent ion not visible, due to poor signal to noise ratio.

Scheme IV

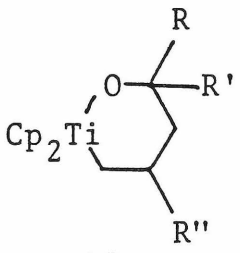


exception of particularly labile acetylenes, the formation of 6 from 2 appears to be well established, and perhaps CO insertion and removal from titanium will be equally general. Work remains to be done to determine which functional groups (on R, R', R", and R"') will not interfere with the course of the reaction, whether or not a one-pot synthesis can be effected, optimum reaction conditions, and how widely applicable the scheme is, but the approach is an attractive one.

The reaction of titanacyclobutenes with carbonyl compounds is, on the basis of a few preliminary experiments,

second order (first order in titanacyclobutene, first order in carbonyl). Carbonyl compounds which typically show sharp resonances in the NMR show instead broadened signals in the presence of titanacyclobutene; when the reaction has gone to completion, any excess carbonyl compound again shows a sharp resonance, suggesting that the carbonyl is reversibly binding to 2 before reaction. The reaction shows a solvent dependence (the reaction is approximately ten times faster in THF than in benzene).

III. Reaction of Titanacyclobutanes and Heteroatom-Carbon Double Bonds. Grubbs[5] has reported that the alkene (3,3-dimethyl-1-butene) can be displaced from titanacyclobutane 3a by diphenylacetylene or Me_2AlCl. We investigated the possibility that alkene might also be displaced by carbonyl to give oxytitanacyclobutane 5 or that insertion might occur to give an oxytitanacyclohexane 10. All investigations along these lines were performed with 3a, the most stable titanacyclobutane to date.



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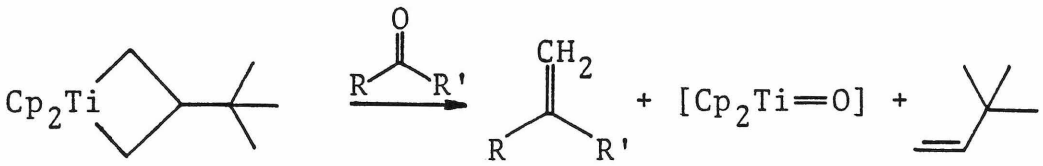
Compound 3a, with all organic carbonyl compounds tested, gives the alkene product of methylene for oxygen exchange in good yield (Reaction 10). Yields are listed in Table 5. Ketone and ester substrates react with one-



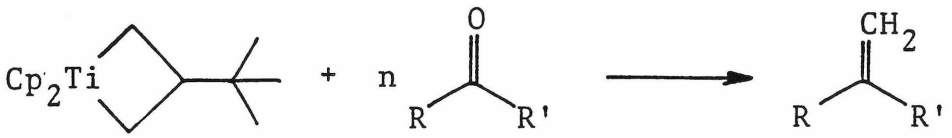
Reaction 10

to-one stoichiometry, while two equivalents of aldehyde substrate are required for complete reaction of 3a. This also is shown in Table 5. The organometallic product is titanocene oxide polymer, an intractable yellow solid described in the literature.[17] It is presumably formed from mononuclear titanocene oxide, although the intermediacy of this is not directly observed. 3,3-Dimethyl-1-butene (100% per Ti) is also produced.

Compound 3a also reacts with C=N double bonds, but the yield is much poorer than reactions with C=O double bonds (Reaction 11).

The mechanism of the reaction between 3a and carbonyl is of interest, especially since one might expect some common intermediates in this and other reactions of 3a and perhaps even of 1. This will be discussed below.

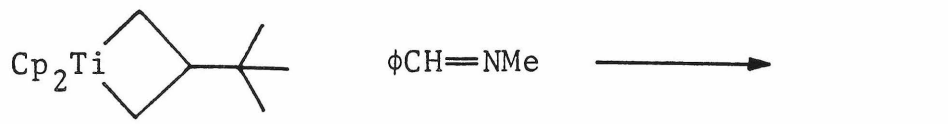
Table 5. Reactions of 3a With Carbonyl Substrates.



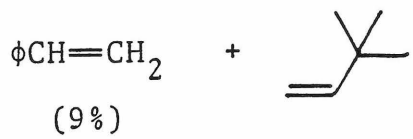
3a

Substrate	Product (Yield per Ti)	Equivalents Required (n)
acetone	isobutylene (90%)[a]	1
benzaldehyde	styrene (92%)[b]	2
acetophenone	α-methylstyrene (94%)[a]	1
trimethyl-acetaldehyde	3,3-dimethyl-1-butene[a] (100%)	2
methyl benzoate	α-methoxystyrene (90%)[b]	1

a) NMR yield. b) Yield by gas chromatography.

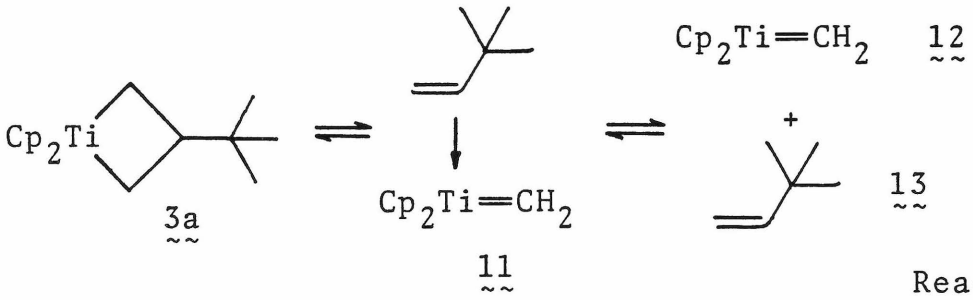


Reaction 11



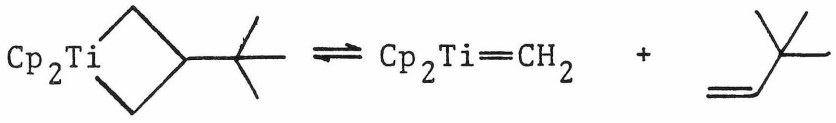
(9%)

IV. Mechanism of the Reaction Between 3a and Carbonyl Compounds. One can envision a number of mechanisms for the reaction between 3a and a carbonyl substrate. Several reactive organometallic intermediates, including a titanocene carbene 12, are suggested by analogy to the proposed olefin metathesis mechanism (References 2, 3, and 4, and see also Scheme I), and they are certainly in equilibrium, either with or without the intermediacy of carbene-olefin complex 11 as a discrete intermediate (Reactions 12 and 13). Compound 3a and/or



3a 11 12 13

Reaction 12

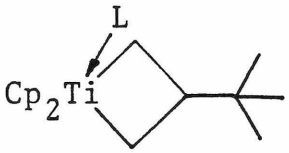


3a 12 13

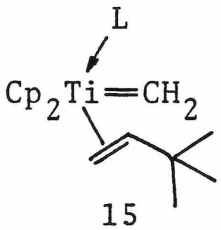
Reaction 13

any of these intermediates might react with carbonyl substrate to yield alkene. In the presence of added 3,3-dimethyl-1-butene 13, carbonyl, solvent, or another potential ligand, several other species are also possible (14, 15, and 16, for instance), and these may also be

species which are important in the mechanism. Steric requirements for 14 may be severe,[18] and 15 is formally a 20-electron species (although one could argue that a Cp ring has backed off from η^5 to η^3 to alleviate this situation). When L = 13, 16 is, of course, 11 in Reaction 12. Depending on the rate-determining step, one might see first or second order kinetics, or one might observe



14



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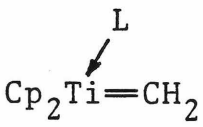


16

some intermediate species. Derivation of kinetic expressions to describe various mechanisms is possible, but before further discussion we shall narrow the field somewhat by considering some of the data.

Kinetic data have been obtained by following the reaction between 3a and a carbonyl substrate by NMR. Compound 3a reacts at approximately (± 20%) the same rate with all carbonyl substrates (Table 6). The reaction rate is nearly independent of carbonyl concentration (from one to fourteen equivalents) and shows first order kinetics

Table 6. Rates of Reaction of 3a With Various Substrates.

Substrate (Concentration, M)	Rate (Temperature, °C)[a] in sec^{-1}
trimethylacetaldehyde (0.44)[b]	1.6×10^{-5} (25)
acetophenone (0.22)[b]	1.5×10^{-5} (25)
methyl benzoate (0.22)[b]	1.3×10^{-5} (25)
acetone (0.72)[c]	2.43×10^{-5} (27)
acetone (13.7)[c]	2.67×10^{-5} (27)
methyl benzoate (0.44)[b]	4.89×10^{-5} (37)
methyl benzoate (0.88)[b]	4.94×10^{-5} (37)
methyl benzoate (1.76)[b]	5.42×10^{-5} (37)
trimethylacetaldehyde (0.36)[c]	9.3×10^{-5} (40)
trimethylacetaldehyde (0.72)[c]	9.8×10^{-5} (40)
trimethylacetaldehyde (1.54)[c]	10.7×10^{-5} (40)

a) Plotted as first order in 3a, zero order in substrate. See also Footnote 19. b) [3a] = 0.22 M. c) [3a] = 0.36 M.

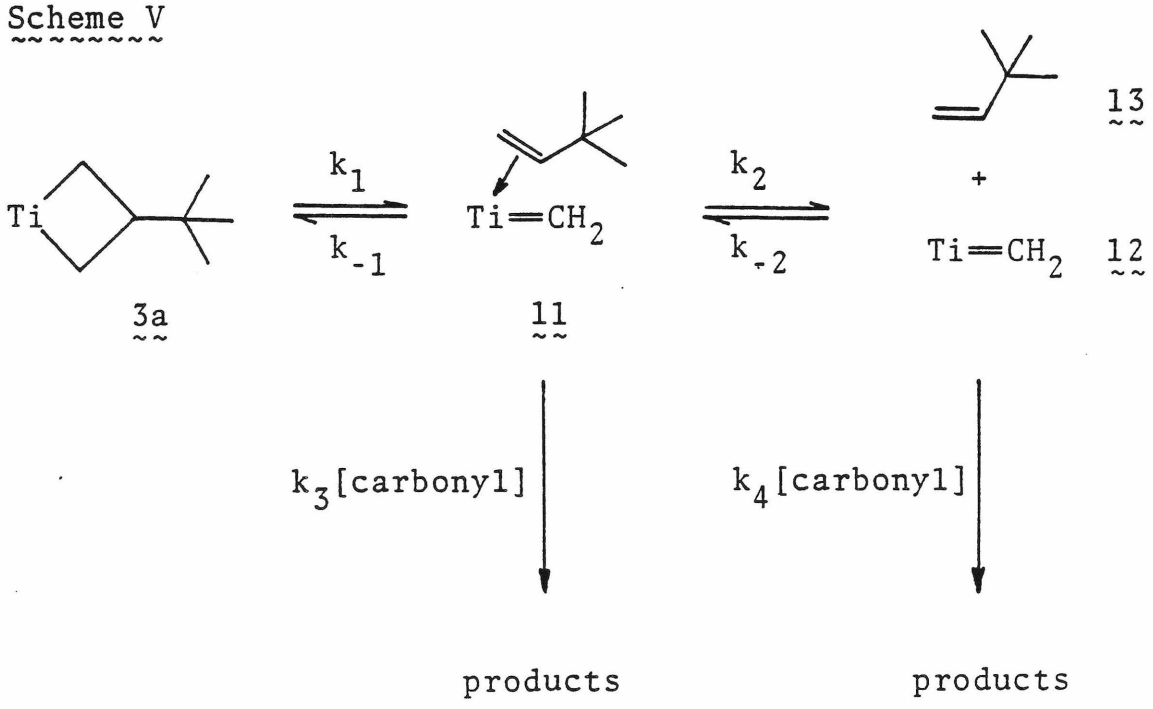
for the disappearance of 3a for greater than one half-life.[19] The reaction is independent of solvent, with approximately the same rates being observed in benzene and THF. Other workers have observed similar rates and kinetics (first order in 3a, zero order in substrate) with acetylenes.[12] No new species are observed to grow in and then disappear (except, of course, that one observes the final products, 13 and the alkene from methylene for oxygen exchange, growing in).[20]

The NMR spectra of 3a are the same in the presence or absence of carbonyl substrate, added alkene 13, or pyridine. The NMR resonances for the carbonyl substrates remain sharp and are not shifted in the presence of 3a. This suggests that one is not rapidly forming a complex such as 14 (L = carbonyl compound) and then actually observing the disappearance of the complex. Furthermore, one might expect an observed rate of disappearance of 14 to vary greatly as carbonyl ligand L varies[21] (from ketones to esters, and small to bulky substrates), and this is not observed. Similar arguments apply to 15 and 16. The first order kinetic data rule out a reaction between 3a and carbonyl (or between any species and carbonyl) in the rate-determining step.

This leaves us with the following possibilities: either 11 or 12 or both are trapped by carbonyl, and the

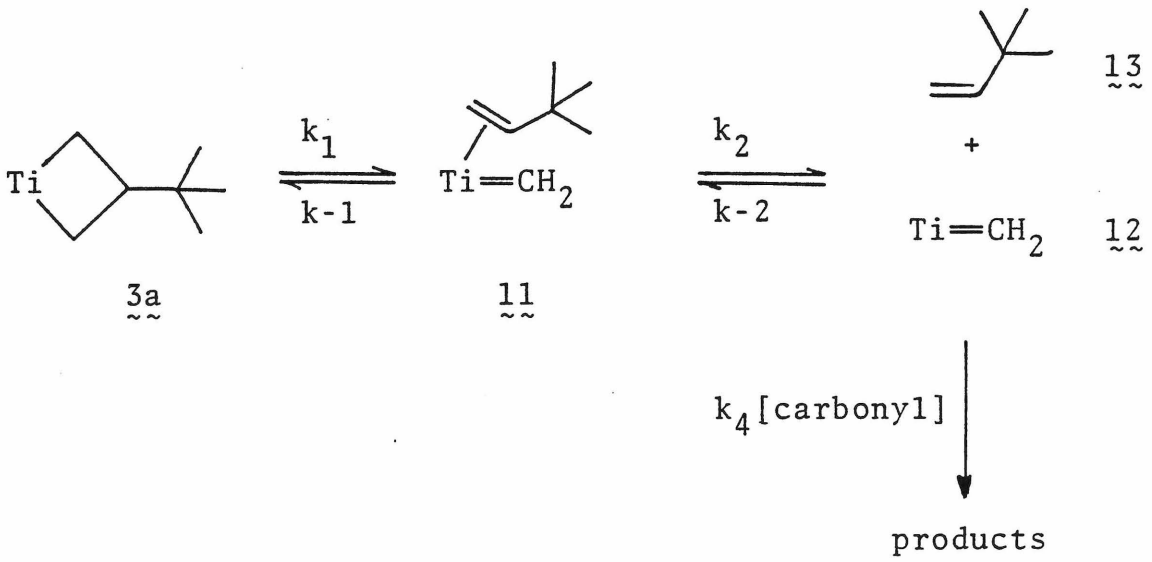
rate-determining step is formation of 11 from 3a or of 12 from 11, as long as it occurs before trapping by carbonyl (Scheme V, Cases 1 through 4). Trapping of 11 by carbonyl will involve 15 as either a transition state or an intermediate further along the reaction pathway; similarly, trapping of 12 leads to 16. Little can be learned about these from the experimental data, since only the starting materials and final products can be observed, but such intermediates will be discussed later (vide infra).

Scheme V



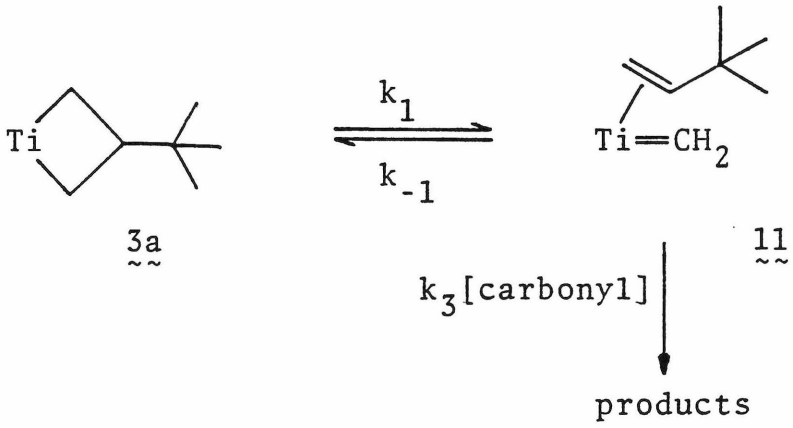
Notes: Cp rings omitted. Depending on relative rates and the rate-determining step, the following cases are envisioned:

Case 1: k_3[carbonyl] << k_{-1} or k_2, so that no trapping of 11 by carbonyl occurs. k_1 or k_2 can be rate-determining.



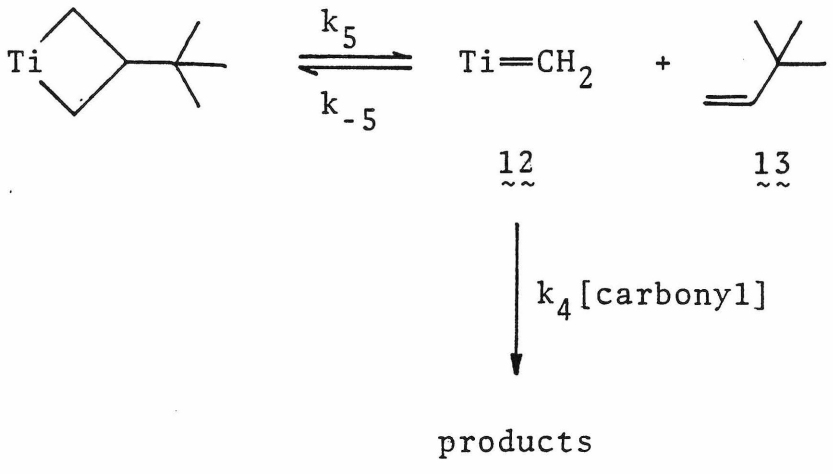
Case 2: k_2 << k_3[carbonyl] or k_{-1}, so that no free carbene 12 is formed or trapped. k_1 is rate-determining. Actually, one obtains identical kinetic expressions with or without including the equilibrium between 11 and 12, if trapping of 12 does not occur (although it seems unlikely that 12 would not be trapped by carbonyl), and

both of these possibilities are derived in Appendix I, to prove this.



Case 3: Trapping of both 11 and 12 occurs, just as shown in Scheme V. k_1 or k_2 rate-determining, but to see first order kinetics, k_3[carbonyl] must be negligible if k_2 is rate-determining. Mixed kinetics are possible.

Case 4: Compound 3a might be directly in equilibrium with 12, which is trapped by carbonyl. We must now assign different rate constants, since we are talking about different reactions. k_5 is rate-determining.



For the present, we will just consider trapping of 11 and 12 to lead to products with a rate k_3 or k_4, respectively, which represents the overall rate of the reaction (i.e., the rate-determining step) and which is assumed to be second order (first order in 11 or 12, and first order in carbonyl). The various mechanisms are given in Scheme V, Cases 1 through 4, and kinetic expressions have been derived for each of these in Appendix I. While the reactions with rate constants k_3 and k_4 in these schemes cannot be rate determining (or second order kinetics would be observed), they may be either comparable

to or much faster than competing reactions.

If $\underset{\sim\sim}{12}$ (titanium carbene from which alkene $\underset{\sim\sim}{13}$ has dissociated) is (one of) the intermediates which is trapped (Cases 1, 3 or 4) and if $k_{-2}[\underset{\sim\sim}{13}]$ or $k_{-5}[\underset{\sim\sim}{13}]$ is competitive with k_4[carbonyl] then addition of alkene $\underset{\sim\sim}{13}$ to the reaction mixture should slow the formation of products and the disappearance of $\underset{\sim\sim}{3a}$. Indeed, when methyl benzoate is the carbonyl substrate, we do observe that the rate of disappearance of $\underset{\sim\sim}{3a}$, while still best fitting first order kinetics, shows a slight decrease (Table 7). Therefore, methyl benzoate must be trapping $\underset{\sim\sim}{12}$ and k_4[carbonyl] and $k_{-2}[\underset{\sim\sim}{13}]$ or $k_{-5}[\underset{\sim\sim}{13}]$ must be competitive. Methyl benzoate may also be trapping $\underset{\sim\sim}{11}$. However, one would expect trapping of $\underset{\sim\sim}{11}$ (which is formally 18-electron) to be considerably slower than trapping of $\underset{\sim\sim}{12}$ (which is 16-electron) for a given substrate. Let us make the approximation that methyl benzoate (=MB) traps only $\underset{\sim\sim}{12}$ (Cases 1 or 4). We can then do the following experiment: using large amounts of $\underset{\sim\sim}{13}$ and MB relative to $\underset{\sim\sim}{3a}$ (so that the concentrations of $\underset{\sim\sim}{13}$ and MB can be assumed to remain approximately constant during the first half-life of the reaction), we can vary from sample to sample the ratio of $\underset{\sim\sim}{13}$ to MB, and obtain for each sample an observed rate constant k_{obs} by plotting the first order disappearance of $\underset{\sim\sim}{3a}$. For Case 1 ($\underset{\sim\sim}{12}$ is formed from $\underset{\sim\sim}{11}$, and $\underset{\sim\sim}{12}$ is

trapped by carbonyl)

$$k_{obs} = k_1 \left\{ \frac{k_2 k_4 [MB]}{k_4 [MB](k_{-1} + k_2) + k_{-1} k_2 [\underset{\sim}{\underset{\sim}{13}}]} \right\}$$

or

$$\frac{k_1}{k_{obs}} = \left\{ 1 + \frac{k_{-1}}{k_2} \right\} + \left(\frac{k_{-1} k_{-2}}{k_2 k_4} \right) \frac{[\underset{\sim}{\underset{\sim}{13}}]}{[MB]}$$

We can plot k_1/k_{obs} *vs* $[\underset{\sim}{\underset{\sim}{13}}]/[MB]$ and obtain a plot with intercept $(1 + k_{-1}/k_2)$ and slope $(k_{-1}k_{-2})/k_2k_4$. To do this, of course, we need a value for k_1. For Case 4 (where $\underset{\sim}{\underset{\sim}{12}}$ is formed directly from $\underset{\sim}{\underset{\sim}{3a}}$, and $\underset{\sim}{\underset{\sim}{12}}$ is trapped)

$$\frac{1}{k_{obs}} = \frac{1}{k_5} + \left(\frac{k_{-5}}{k_5 k_4} \right) \frac{[\underset{\sim}{\underset{\sim}{13}}]}{[MB]}$$

and a plot of $1/k_{obs}$ *vs* $[\underset{\sim}{\underset{\sim}{13}}]/[MB]$ yields a plot with intercept $1/k_5$ and slope k_{-5}/k_5k_4.

When $\underset{\sim}{\underset{\sim}{3a}}$ is allowed to react with a mixture of excess acetone and excess methyl benzoate, the sole product observed (by NMR or gas chromatographic analysis) is isobutylene, indicating that acetone traps the reactive

organometallic intermediate(s) at least 100 times faster than methyl benzoate. This is consistent with the observations made by Pine for $\underset{\sim}{1}$: $\underset{\sim}{1}$ reacts much more rapidly with acetone than methyl benzoate does.[21] We have also generated $\underset{\sim\sim}{12}$[22] in the presence of acetone and methyl benzoate (by adding a mixture of excess pyridine, acetone and methyl benzoate to $\underset{\sim}{1}$), and again observed acetone to react at least 100 times faster. Since we are seeing what appear to be first order kinetics for the disappearance of $\underset{\sim\sim}{3a}$ even in the presence of only low concentrations of methyl benzoate, we can assume that in high concentrations of acetone, trapping is very efficient, and we can use the approximation that $k_1 \cong k_{obs}$ when the reaction is followed in neat acetone-d_6.

The observed rates at varying ratios of [$\underset{\sim\sim}{13}$]/[MB] are contained in Table 7. Following Case 1 (trapping only $\underset{\sim\sim}{12}$, where $\underset{\sim\sim}{12}$ is formed from $\underset{\sim\sim}{11}$) and using the approximate value of k_1 obtained in neat acetone-d_6, the plot of k_1/k_{obs} versus [$\underset{\sim\sim}{13}$]/[MB] yields an intercept of 1.57 and a slope of 0.284, which leads to the following:

$$\frac{k_{-1}}{k_2} = 0.57 \qquad \frac{k_{-2}}{k_4} = \frac{0.284}{0.57} = 0.50$$

Table 7. Observed Rates of Disappearance of 3a in the Presence of Varying Amounts of Methyl Benzoate and Alkene 13.[a],[b],[c]

Sample #	[13]	[MB]	[13]/[MB]	k_{obs}, sec^{-1}
	M	M		
1	2.42	1.21	2.00	2.50×10^{-5}
2	2.42	2.42	1.00	2.85×10^{-5}
3	1.21	1.21	1.00	2.82×10^{-5}
4	2.42	3.63	0.67	2.98×10^{-5}
5	1.21	2.42	0.50	3.17×10^{-5}

a) Plotted as first order for the disappearance of 3a. b) At 31.5°C. [3a] = 0.242 M. c) k_{obs} in neat acetone-d_6 = 4.98×10^{-5} sec^{-1} at 31.5°C.

This is consistent with our assumption that k_{-2} and k_4 are competitive. If we follow Case 4 (12 is trapped after being formed directly from 3a), we obtain an intercept of 2.97×10^4 sec, and a slope of 5.37×10^3 sec, which gives us

$$k_5 = 3.37 \times 10^{-5} \text{ sec}^{-1} \qquad \frac{k_{-5}}{k_4} = 0.181$$

This also gives a result consistent with our assumption of competitive k_4 and k_{-5}. However, it is impossible for k_5 to be 3.37×10^{-5} sec^{-1} if we have already observed faster reactions when acetone is the substrate, as there is no way the reaction can proceed faster than k_5 (the rate-determining step), no matter how efficiently and rapidly we trap $\underset{\sim\sim}{12}$. This suggests that Case 4 is incorrect, and further experimentation will support this contention (vide infra).

If acetone reacts much more rapidly with $\underset{\sim\sim}{12}$ than methyl benzoate does (k_4' for acetone >> k_4 for methyl benzoate),[23] it is reasonable to suppose that acetone also reacts much more rapidly with $\underset{\sim\sim}{11}$ than methyl benzoate (k_3' for acetone >> k_3 for methyl benzoate). Case 1, in which carbonyl substrate traps only $\underset{\sim\sim}{11}$ is now (possibly) insufficient to describe the reaction of 3a with acetone, so we must consider Cases 2 (in which carbonyl traps $\underset{\sim\sim}{11}$) and 3 (in which carbonyl traps $\underset{\sim\sim}{11}$ and $\underset{\sim\sim}{12}$). Case 2 will apply only if acetone traps $\underset{\sim\sim}{11}$ so rapidly that $\underset{\sim\sim}{12}$ never has a chance to form ($k_2[\underset{\sim\sim}{11}] << k_3[\underset{\sim\sim}{11}][\text{acetone}]$).

We can do the following experiment: a large excess of acetone (such that the concentration remains approximately constant over the course of the first half-life) can be used in each sample, with the concentration of acetone varying from sample to sample. The rate constants

for this experiment are given in Table 8.

If we assume for a moment that acetone traps $\underset{\sim\sim}{11}$ so rapidly that $\underset{\sim\sim}{12}$ never has a chance to form, then we can use Case 2 to describe our system, and the rate constant observed for disappearance of $\underset{\sim\sim}{3a}$, k_{obs} for each sample, will be

$$k_{obs} = k_1 \frac{k_3'[\text{acetone}]}{k_{-1} + k_3'[\text{acetone}]}$$

or

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_3'k_1[\text{acetone}]}$$

and a plot of $1/k_{obs}$ versus 1/[acetone] gives a plot with intercept $1/k_1$ and slope $k_{-1}/k_3'k_1$. From the intercept of 1.94×10^4 sec, we obtain a value for k_1[24] of

$$k_1 = 5.15 \times 10^{-5} \text{ sec}^{-1}$$

and the slope (1.68×10^4 sec·M) yields a value for k_{-1}/k_3' of

$$\frac{k_{-1}}{k_3'} = 0.87 \text{ M}$$

Table 8. Observed Rates of Disappearance of 3a in the Presence of Varying Amounts of Acetone-d_6.[a,b]

Sample #	[acetone], M	k_{obs}, sec^{-1}
1	13.7	4.98×10^{-5}
2	6.85	4.76×10^{-5}
3	3.65	4.36×10^{-5}
4	2.42	4.21×10^{-5}
5[c]	6.85	4.9×10^{-5}
6[c]	2.42	4.3×10^{-5}

a) Plotted as first order for the disappearance of 3a. b) At 31.5°C. [3a] = 0.242 M. c) These samples also contain added alkene, [13] = 3.87 M. Due to the difficulty in integrating somewhat poorly resolved peaks in the NMR in the presence of large amounts of 13, these rate constants are somewhat less accurate than those determined for Samples 1 through 4, and so k_{obs} is only expressed to two significant figures.

Since we know from the methyl benzoate work that k_{-1}/k_2 = 0.57, we can determine that

$$\frac{k_3'}{k_2} = 0.66\ M^{-1}$$

In neat acetone-d_6 (13.7 M), $k_3'[acetone]/k_2$ is, therefore,

9.04/1, so our use of Case 2 to describe the reaction in neat acetone-d_6 is certainly reasonable.

If we are to be rigorous, however, we should instead consider Case 3 in which both $\underset{\sim\sim}{11}$ and $\underset{\sim\sim}{12}$ are trapped by acetone [i.e., k_3,[acetone] is not so much greater than k_2 that we can neglect k_2]. We know that k_{-2}/k_4 for methyl benzoate is 0.50, and that k_4,[acetone]/k_4[MB] is at least 100.[23] In deriving kinetic expressions for Case 3, therefore, we can use the fact that $k_4' >> k_2$, and make some simplifications. We then obtain:

$$k_{obs} = k_1 \left\{ \frac{k_2 + k_3,[\text{acetone}]}{k_2 + k_{-1} + k_3,[\text{acetone}]} \right\}$$

or

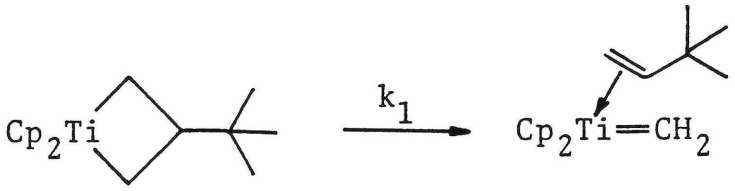
$$\left(\frac{k_1}{k_{obs}} - 1 \right)^{-1} = \left(\frac{k_{-1}}{k_2} \right) + \frac{k_3,[\text{acetone}]}{k_{-1}}$$

Using the value of k_1 observed above (since this is our best number for this rate constant) we can plot $(k_1/k_{obs} - 1)^{-1}$ versus [acetone] to obtain values for k_{-1}/k_2 (the intercept) and k_3/k_{-1} (the slope). Since the difference between k_1 and k_{obs} is very small, there is a large amount of error in this determination, but it is encouraging to note that the numbers so obtained:

$$\frac{k_{-1}}{k_2} = 0.26 \qquad \frac{k_3}{k_{-1}} = 1.74$$

are qualitatively in agreement with those values which we had determined previously.

Since the observed rate in neat acetone-d_6 is, within experimental error, k_1, we can now determin E_a and $\Delta S^{\ddagger}$ for Reaction 14 by determining k_1 at various temperatures.



Reaction 14

3a 11

The rates are listed in Table 9, and a plot of $\log_{10}(k_1)$ versus 1/T (temperature in °K) gives a slope of -4.73 x 10^3 °K and an intercept of 11.2. From this it can be calculated that:

$$E_a = 21.6 \text{ kcal/mole} \qquad \Delta S^{\ddagger} = -9.31 \text{ e.u.}$$

While both of these values are quite reasonable for k_1 in Case 2, 3 or 4, a negative $\Delta S^{\ddagger}$ is inconsistent with a dissociative rate-determining step (such as k_5 in Case 4

Table 9. Observed Rate Constants for the Disappearance of 3a at Various Temperatures.[a]

Sample #	Temperature, °C	k_{obs}, sec^{-1}
1	51.0	4.43×10^{-4}
2	31.5	4.98×10^{-5}
3	27.0	2.67×10^{-5}
4	4.8	1.67×10^{-6}

a) [3a] = 0.242 M, in neat acetone-d_6.

or k_2 in Case 1).

In addition to the competition between acetone and methyl benzoate described above, several other competition experiments were performed, between substrates expected to trap the same intermediate. Relative rates of reaction of two substrates were determined by measuring the relative amounts of products formed from each.

It was assumed that reaction of 1 with pyridine would generate 12 (by removing Me_2AlCl from the coordination sphere of titanium), which could then be trapped with ketone or ester substrates. Two competing esters, when allowed to react with 3a, would also trap 12, so the same relative rates should be observed for competing

esters in either case. Even in the presence of added alkene 13, little or no trapping at 11 is to be expected of esters.

Ketones, however, when allowed to react with 3a, will trap 11, and different ratios of rates might be expected for trapping 11 and 12 (from 1 and pyridine). Added alkene, however, should have no effect on the trapping of 11 (since 11 will never dissociate alkene 13 before being trapped) or 12 (since k_{-2}[13] is so small compared to k_4,k_4,[ketone]).

The results of the competition experiments are shown in Table 10. Observations are as expected. Although steric effects must certainly enter into considerations of the relative rates of reactivity of different substrates, one also sees that rates increase as electron density on oxygen (as a result of more electron-donating groups on the carbonyl group) increases. It appears then that Scheme V describes our system (Scheme V and known relative rates are reproduced below). Methyl benzoate traps only at 12, k_3[MB] being too slow to compete effectively with k_{-1} or k_4 (Case 1). k_4[MB] is the same order of magnitude as k_{-2}[13] in our system, and so a dependence of k_{obs} on [13] is observed. Acetone, on the other hand, can trap at 11 and, at very high concentrations of acetone, neither k_{-1} nor k_2 can compete effectively with k_3,[acetone] (Case 2 applies). Acetone will also trap 12 (if 12 has a chance to

Table 10. Competition Experiments.

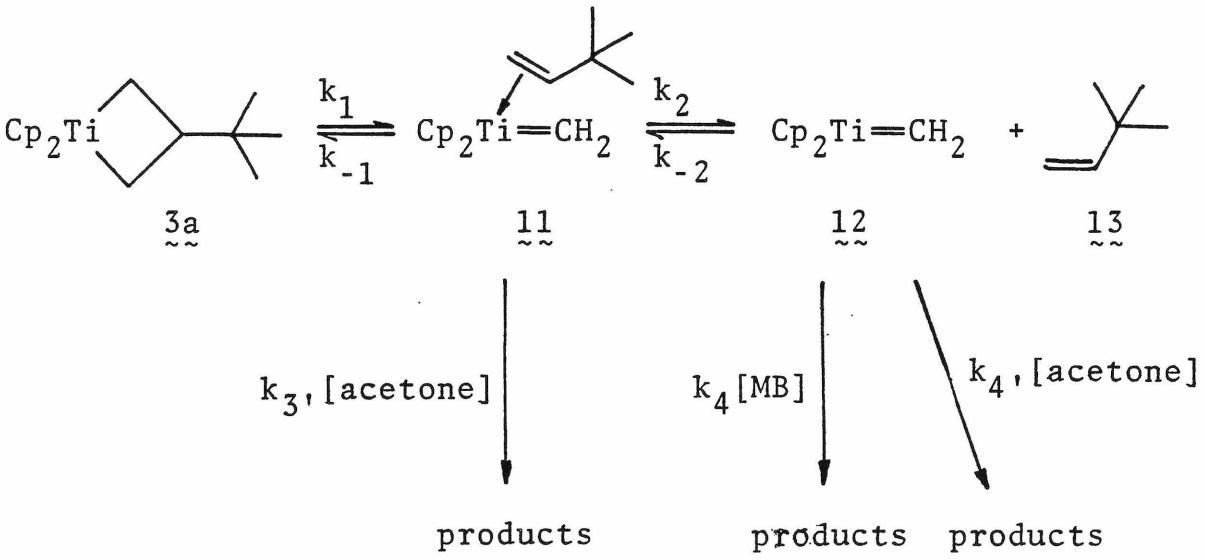
Substrate A	Substrate B	Reactive Ti Species	[13]^{a} M	Rate A / Rate B
Acetone	Acetophenone	11^{b}	0	2.3
Acetone	Acetophenone	11^{b}	3.9	2.3
Acetone	Acetophenone	12^{c}	0	2.0
Acetone	Acetophenone	12^{c}	3.9	2.1
Ethyl Acetate	Methyl Benzoate	12^{d}	0	13
Ethyl Acetate	Methyl Benzoate	12^{d}	3.9	14
Ethyl Acetate	Methyl Benzoate	12^{c}	0	15
Ethyl Acetate	Methyl Benzoate	12^{c}	3.9	15

a) Concentration of added alkene. This does not include the concentration of 13 produced by reaction of 3a. b) Using Case 2 to approximately describe the reaction of 3a with ketone, the reaction of ketone with 3a will result in the trapping of 11. Small amounts of 12 will also be trapped (Case 3). c) From 1 and pyridine. d) Using Case 1 (or Case 3, with a very small k_3), the reaction of 3a with esters will trap only 12.

form from 11: Case 3), and k_4' is undoubtedly so fast that k_{-2} has no chance of competing with it; and, therefore, no dependence of k_{obs} on alkene concentration is observed.

It would, of course, be very interesting to know k_1/k_{-1} or k_2/k_{-2}. Unfortunately, the present system does not allow

Scheme V



$k_1 = 5.5 \times 10^{-5}$ sec^{-1} at 31.5°C

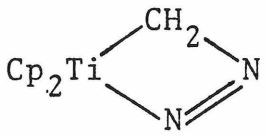
E_a = 22 kcal/mole $\quad \Delta S^{\ddagger} = -9$ e.u.

$$\frac{k_{-1}}{k_2} = 0.57 \qquad \frac{k_{-2}}{k_4} = 0.50$$

$$\frac{k_{-1}}{k_{3'}} = 0.87\ M \qquad \frac{k_{3'}}{k_2} = 0.66\ M^{-1}$$

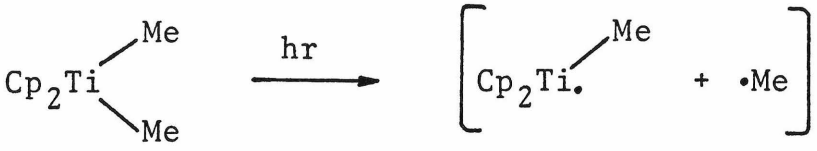
for the determination of these or of any absolute rates (except k_1) because 11 and 12 cannot be directly observed. (Examination of the kinetic expressions will reveal that all one can determine from such a system is the relative rates

of any two reactions which compete for a given intermediate.) Alternate approaches might, however, yield such information. If one could generate 12 in known concentrations and watch its disappearance (or the formation of products from 12 and some other substrate) one could learn k_4. We have attempted to generate 12 from 1 and pyridine at low temperatures and then follow the subsequent reactions by NMR, but the spectral resolution is too poor to allow one to succeed in this approach.[25] Another means to 12 might be to synthesize a diazo compound such as 17, which could perhaps easily loose N_2 and generate 12. Work along these lines is proceeding in our laboratories.



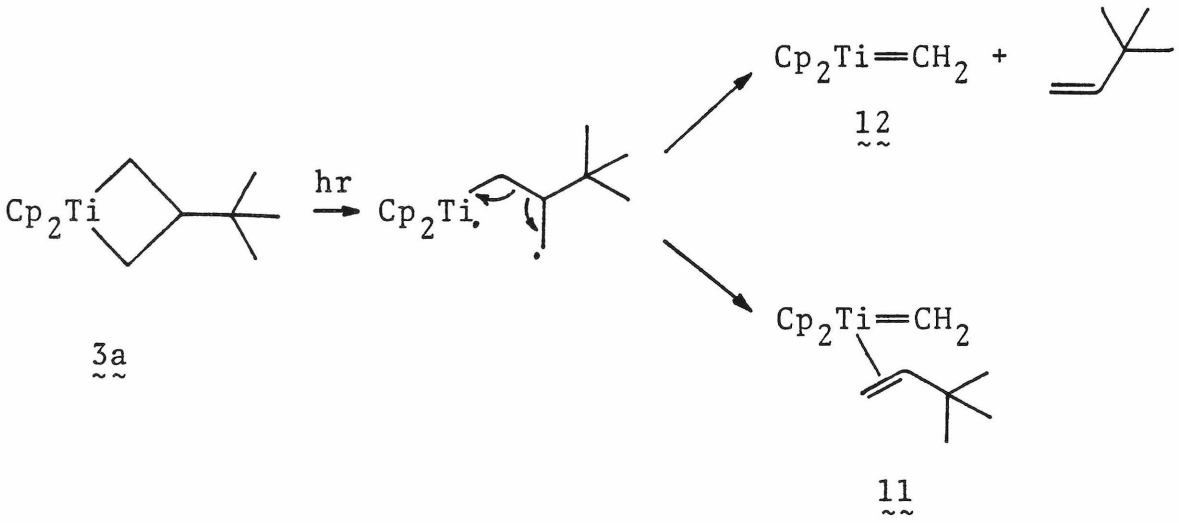
17

Photochemical approaches may also hold some promise: disappearance of 3a in neat acetone-d_6 at -20°C is two to three orders of magnitude faster when the reaction is irradiated with unfiltered ultraviolet light. Work by several workers[26] on the photochemistry of Cp_2TiMe_2 and related compounds suggests that the initial photoproducts are radicals (Reaction 15), so that (if we are seeing

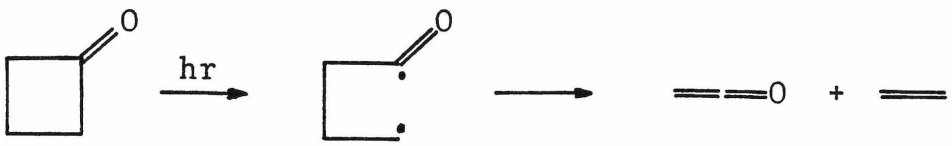


Reaction 15

photochemistry from an excited state of 3a rather than attack by an n → π* state of acetone) we might initially expect to form a 1,4-diradical which might then lead to 11 or 12 (Reaction 16). The formation of double bonds from an organic 1,4-diradical is well established for cyclobutanones (Reaction 17),[27] and ethylene has been observed in the photodecomposition of platinocyclobutanes.[28]



Reaction 16

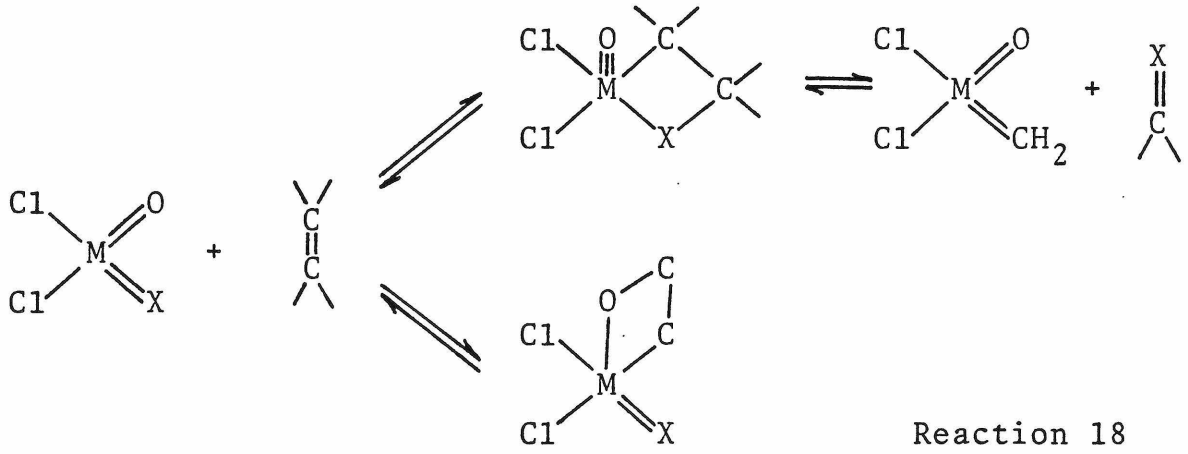


Reaction 17

One could perhaps distinguish between the photoproducts (i.e., between 11 and 12) on the basis of competition experiments: since the relative rates of reaction of two ketone substrates with 11 and 12 are known and are different, the product ratio from irradiation ought to reflect the photochemically formed intermediate. Ketones are ideal for this study since we know they react rapidly with 11 or 12 (this prevents 11, if it is formed photochemically, from going to 12 before being trapped). One might also be able to directly observe the photoproduct (by generating it in high concentrations via flash photolysis) and watch its rate of disappearance in the presence of a reactive substrate. A great deal might be learned from such a study.

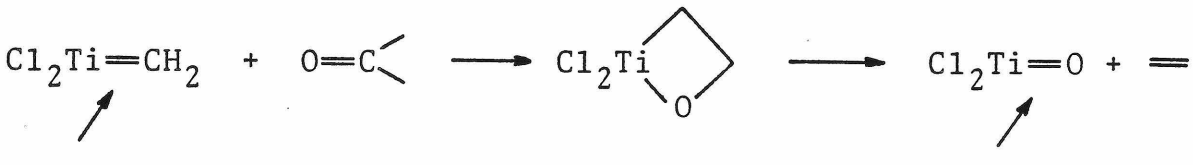
Another approach is to tackle the system with theoretical studies. Rappé and Goddard[29] have reported calculations on

molybdenum and chromium systems. The M=O bonds in these systems strongly direct the course of the reactions (Reaction 18), and therefore a good analogy to our titanium



Reaction 18

system cannot be made. Work is in progress to calculate the corresponding titanium reactions (Reaction 19), but it is not yet completed.[30] However, rough initial estimates of bond energies[30] indicate that the overall sequence of $\underset{\sim\sim}{12}$ going to products ought to be exothermic (by 28-30 kcal/mole, if one uses bond energies of $O{=}CH_2$ = 175 kcal/mole and $H_2C{=}CH_2$ = 163 kcal/mole).[31] While one might predict that

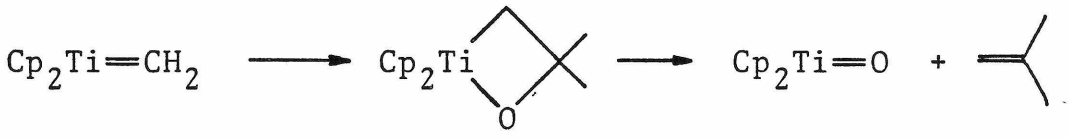


70-80 kcal/mole

120 kcal/mole

Reaction 19

Reaction 20 ought to be downhill every step of the way (and also rapid), it is premature to draw any conclusions, since so little is known about the metallacyclobutanes or

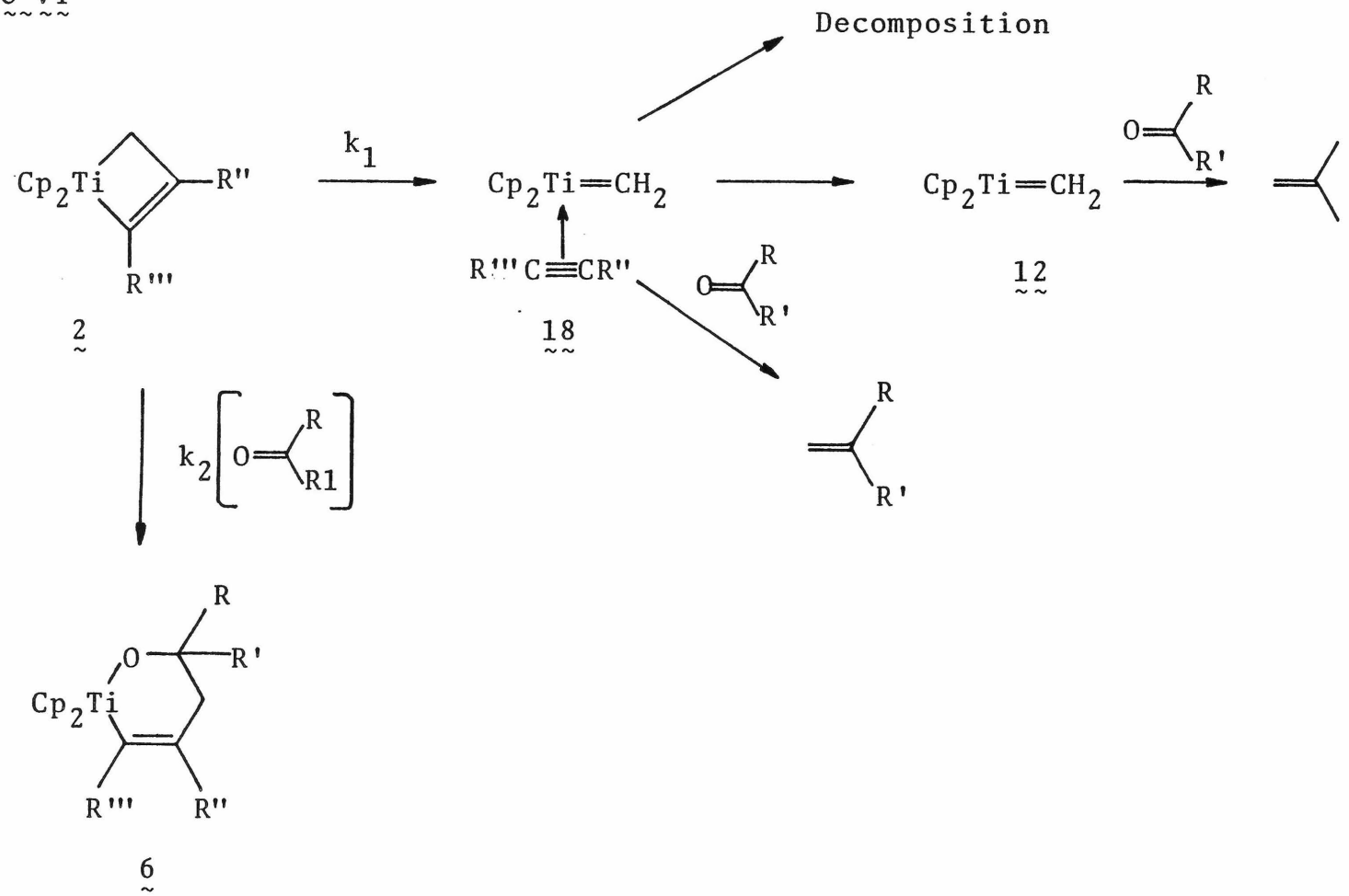


Reaction 20

oxymetallacyclobutanes. Interestingly, Caulton[32] suggests that the alkoxy ligand in $Cp_2Ti(OEt)Cl$ functions as a 3-electron donor; but, it is too early to judge how that fact will be reflected in an oxytitanacyclobutane.

Metallocyclobutenes may form oxymetallacyclohexenes if the formation of a carbene-acetylene complex 18 is much slower than the insertion of the carbonyl compound ($k_1 << k_2$[carbonyl] in Scheme VI). In cases where k_1 is fast, however, some oxygen for methylene exchange may occur, either <u>via</u> trapping of 18 or 12 or both, along with other decomposition reactions. A thorough investigation of these possibilities has not been made.

Scheme VI



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Experimental Section

General. All manipulations (except work-up of organic compounds) were carried out under purified nitrogen in a Vacuum Atmospheres Recirculating Dry Box, under argon using standard Schlenk techniques, or on a vacuum line.

Benzene, toluene, THF, diethyl ether, dimethoxyethane and their deuterated analogs were vacuum transferred from sodium benzophenone ketyl prior to use. Pentane was scrubbed twice with concentrated H_2SO_4, twice with $KMnO_4$ in 10% H_2SO_4, dried, and vacuum transferred from sodium benzophenone ketyl. Acetone was deoxygenated by three freeze-pump-thaw cycles, then dried over 3 Å molecular sieves. Other volatile liquids were deoxygenated by freeze-pump-thawing; high boiling liquids were deoxygenated by pumping directly on the material for 30 min.

Proton NMR spectra were obtained on an EM-390 Varian Associates NMR spectrometer, and IR spectra on a Beckman 4240. Gas chromatographic analyses were performed on a Varian Aerograph Series 1400 GC, using Porapak Q (8' x 1/8" column, 80/100 mesh commercial Porapak Q, 70°C) for C_1-C_4 for hydrocarbon species, Duropak (17' x 1/8", 100/120 mesh, 80°C) for C_2-C_6 species, and Carbowax (6 or 32' x 1/8", Carbowax 20M, 10% on Chromosorb W, AW-DMSC, 100/120 mesh, 80 or 100°C) for larger hydrocarbons or heteroatom-contain-

ing species. Mass spectra were obtained by the Caltech Analytical Laboratory; elemental analyses were performed by the same facility or by Schwarzkopf Microanalytical Laboratory, Woodside, New York.

Preparation of Methylene-Bridged Titanocene Complex 1.[2] Cp_2TiCl_2 (Alfa Division, Ventron Corporation) was recrystallized from toluene, using a soxhlet extractor, in air. To the clean Cp_2TiCl_2 so obtained (24.9 g, 0.1 mol) was added Me_3Al (110 mL of 2 N Me_3Al in toluene, 0.11 mmol) under an inert atmosphere. The reaction mixture was allowed to stir at ambient temperature for 68 h; as CH_4 is evolved, it was necessary to vent the reaction flask through a mercury bubbler. In the dry box, the reaction solution was filtered through a medium frit (this could also be accomplished using Schlenk techniques) and cooled to -40°C. A solid mass of crystals formed; these were broken into small fragments and collected by filtration. The 1 so obtained was not entirely pure, containing traces of $Cp_2\overline{Ti\text{-}CH_2\text{-}Al(Me)(Cl)\text{-}Cl}$ and was recrystallized from toluene/pentane containing a few percent of Me_3Al by cooling to -40°C. The red crystals were collected by filtration, washed with pentane, and dried under vacuum. Yield: 10.0 g (25%) of 1. The mother liquors from the procedures above contained significant amounts of 1, which could be recovered by removal of solvent and recrystallization. NMR (C_6D_6):

δ -0.25 (s, 6H, $AlMe_2$), 5.66 (s, 10H, Cp's), 8.35 (s, 2H, methylene).

Preparation of Titanacyclobutene 2a from 1 and Diphenylacetylene.[4] Diphenylacetylene (1.3 g, 7.3 mmol) was dissolved in 10 mL THF, and cooled to -40°C in the dry box freezer. The cold solution was added to 1 (2.0 g, 7.1 mmol), which had also been cooled, and the reaction mixture was stored at -40°C for 36 h. The mixture was warmed to room temperature, the solvent was removed under vacuum, and the resulting solids recrystallized from toluene/pentane at -40°C. Yield: 2.2 g (84%) of dark red needles of 2a. NMR (C_6D_6): δ 3.49 (s, 2H, methylene), 5.74 (s, 10H, Cp's), 6.8-7.4 (m, 10H, phenyl groups).

2b,[4] 2c,[12] and 2e[12] were prepared from 1 and bis-trimethylsilylacetylene, phenylmethylacetylene, and trimethylsilylphenylacetylene, respectively. 2b: NMR (C_6D_6) δ 0.15 (s, 9H, $SiMe_3$), 0.29 [s, 9H, the other $SiMe_3$ (no specific assignment for α or β position for either $SiMe_3$ group); 4.6 (s, 2H, methylene), 5.17 (s, 10H, Cp's). 2c: NMR (C_6D_6) δ 1.40 (s, 3H, methyl), 3.09 (s, 2H, methylene), 5.42 (s, 10H, Cp's), 6.7-7.2 (m, 5H, phenyl). 2e: NMR (C_6D_6) δ 0.02 (s, 9H, $SiMe_3$), 4.21 (s, 2H, methylene), 5.35 (s, 10H, Cp's), 6.8-7.3 (m, 5H, phenyl).

Preparation of Titanacyclobutene 2d from 1 and 2-Butyne. 1 (1 gm), 2-vinylpyridine-styrene copolymer

(Aldrich Chemical Company, 1 gm), and 20 mL C_6H_6 were placed in a Schlenk flask. Under argon flow, 1 mL 2-butyne was added, and the reaction was allowed to stir for 24 h at ambient temperature. (The flask was kept under a slight positive pressure of argon and was open to a mercury bubbler, as the initially exothermic reaction made the use of a closed vessel impossible.) The solvent and any remaining 2-butyne were removed under vacuum, and the reaction was worked up in the dry box. The mixture was extracted with benzene (25 mL, 2 portions), the extracts were filtered, and the filtrates were taken to dryness under vacuum. The resulting red-black solids were recrystallized twice from pentane to give a poor yield of 2d (approximately 10%). NMR (C_6D_6): δ 5.54 (10H, s, Cp rings), 3.24 (2H, broad singlet, methylene), 2.16 (3H, broad singlet, Me), 1.55 (3H, s, Me).

Preparation of Titanacyclobutane 3a.[5] Compound 1 (2.2 g, 7.8 mmol) and 2-vinyl pyridine-styrene copolymer (from Aldrich Chemical Company, 2.2 g) were placed in a flask in the dry box. 3,3-Dimethyl-1-butene (2.2 mL, 18 mmol) and then benzene (25 mL) were added, and the mixture allowed to stir for 20 h at ambient temperature. The mixture was filtered through a coarse frit, and the solvent removed from the filtrate. The resulting red-black solids were taken up in pentane (25 mL), the solution

was filtered through a fine frit, and the filtrate cooled to -40°C to produce dark red needles of 3a, which were collected by filtration and dried under vacuum. Yield 1.2 g (57%) of 3a. NMR (C_6D_6): δ 0.02 (m, J = 10 Hz, 1H, H in β-position), 0.97 (s, 9H, t-butyl), 1.94 and 2.26 (non-first order d of d, J = 10 Hz, total of 4 H, H's in α-position), 5.43 and 5.64 (s, 5H each, Cp's). For all kinetic work, 3a was recrystallized one more time, from pentane.

Reaction of 1 With N-Benzylidenemethylamine. Compound 1 (28 mg, 0.1 mmol), N-benzylidenemethylamine (12.3 µl, 0.1 mmol), and anisole (10.8 µl, 0.1 mmol), as internal standard) were placed in 330 µl of C_6D_6 in an NMR tube. The tube was sealed, and the reaction followed by NMR. All 1 had disappeared in 5 h, by which time the NMR resolution was very poor. No new organometallic products could be observed. The yield of methylene for NMe exchange product, styrene, was determined by gas chromatography on a 6' Carbowax column (25% per Ti). 37% of the starting N-benzylidenementhylamine remained.

An identical NMR tube to which pyridine was added (8.1 µl, 0.1 mmol, syringed in immediately after all other materials had been mixed) showed immediate disappearance of 1, no new organometallic products, styrene (38% per Ti), and remaining N-benzylidenemethylamine (51%).

Reaction of 1 With Carbonyl in the Presence of Pyridine. Compound 1 (56 mg, 0.2 mmol) was placed in toluene-d_8 (300 µl) in an NMR tube, and cooled to -78°C. An equimolar mixture of pyridine and trimethylacetaldehyde (35 µl, 0.2 mmol of each) was added, and the tube was then sealed. Following the reaction at -60°C in the NMR probe, one observed 3,3-dimethyl-1-butene growing in, and then some 3a forming. No other organometallic products were observed.

Similar results were obtained when the reaction was allowed to proceed at higher temperatures (up to 0°C), except that slightly less 3a was observed.

In another experiment, pyridine (70 µl, 0.88 mmol) was added over 15 min to a stirred solution of 1 (125 mg, 0.44 mmol) in 1 mL of toluene at -78°C. The initially deep red solution had changed to an orange-red solution by the end of the addition, and a precipitate had formed. After stirring at -78°C for 15 min more, acetaldehyde (25 µl in 1 mL toluene, 0.44 mmol) was added slowly, and stirred for 60 min. Gas chromatographic analysis of the volatile components of the reaction mixture showed the presence of propene, indicating that a reactive titanocene carbene of some kind remained after addition of pyridine to 1, for at least 15 min at -78°C. No oxymetallacyclo-

butane could be observed in or isolated from the reaction mixture, however.

Reaction of 1 With CO. Compound 1 (20 mg, 0.070 mmol) was placed in an NMR tube with 500 µl C_6D_6. The solution was freeze-pump-thawed to remove all gases dissolved in solution, then placed under approximately 1 atm of CO gas and sealed (approximately 0.15 mmol CO). The reaction was followed by NMR, and $Cp_2Ti(Me)Cl$ could be observed to grow in several hours; within several days, no organometallic products could be observed in the NMR (including $Cp_2Ti(Me)Cl$, which apparently had decomposed). The organic products in the gas phase and in solution were observed by gas chromatography on Porapak Q and Duropak, and included CH_4, C_2H_4, C_2H_6, propene, isobutylene, and other C_4 and higher hydrocarbons, but not ketene, allene, acetylene or neopentane.

In other runs, the composition of the hydrocarbon mixtures formed in the reaction varied. From a larger scale reaction (1 g 1 in 25 mL C_6H_6 under 1 atm CO in 250 mL flask), $Cp_2Ti(Me)Cl$ was isolated after 20 h of reaction time by removing all solvent under vacuum. The remaining red solids were nearly pure $Cp_2Ti(Me)Cl$, identified by comparison of NMR spectrum and m.p. to literature values.[11]

Reaction of 2 With Carbonyl Compounds. Reactions of the various titanacyclobutenes with carbonyl compounds were all carried out in the same manner; the reaction of 2a with acetone on NMR tube and preparative scales are given as examples.

6a. 2a (19 mg, 0.05 mmol) and acetone (4 µl, 0.05 mmol) were placed in 330 µl C_6D_6 in an NMR tube. The tube was capped, and the reaction followed by NMR. Initially, the acetone resonance was very broad and the solution was deep red; within 48 h, however, the solution had turned yellow-orange, a small amount of remaining acetone showed a sharp NMR signal, and all 2a had disappeared. A quantitative yield of 6a was observed.

On a preparative scale, 2a (1 gm, 2.7 mmol), and acetone (211 µl, 2.7 mmol) were dissolved in 25 mL C_6H_6, and allowed to stir for two days. The solvent was removed under vacuum, and the orange solids so obtained recrystallized from toluene/pentane at 40°C. Yield: 0.87 gm (75%) of yellow-orange crystals of 6a. Calcd. C, 78.50%; H, 6.59; Ti, 11.18. Found: C, 78.91; H, 6.69; Ti, 11.18. Calcd. MW: 428; Found: 436. Mass spectrum: m/e 428 (parent ion), 178 (titanocene). NMR data is included in Table 1 (see text).

6b and 7. A preparative scale reaction between 2a

(1 gm, 2.7 mmol) and benzaldehyde (287 µl, 2.7 mmol) yielded, upon recrystallization from toluene/pentane, small orange crystals and several large dark red crystals. These were separated physically. The orange crystals were recrystallized again from toluene/pentane to yield 0.70 gm (55%) of yellow-orange 6b. Calcd. C, 80.67; H, 5.92; Ti, 10.05. Found: C, 80.76; H, 6.04; Ti, 10.00.

The dark red crystals were scraped free of small orange crystals of 6a, although the NMR spectrum of them still showed small amounts of 6a as contaminant. These were identified as isomer 8 on the basis of their NMR spectrum, color and HCl decomposition products, which have been included in the text in Table 3.

HCl Decomposition of 6. Compound 6a (115 mg, 0.24 mmol) was placed in 3 mL Et_2O in a round-bottom flask containing a stir bar; the flask was capped with a serum cap. 25 mL of HCl gas (1 mmol) was injected via syringe, and the mixture was allowed to stir for 15 min at ambient temperature. The color changed from orange to purple to pale red, with the formation of large amounts of red precipitate. The mixture was worked up in air: the red solid was collected by filtration through a fine frit, and the filtrate taken to dryness on a rotary evaporator. The red solid is Cp_2TiCl_2 (m.p. 280-285°C), 102 mg (88%).

The white solid obtained from the filtrate is the expected organic product of HCl decomposition (see text for NMR, IR and mass spectral data, Table 2), 116 mg (98%). Calcd.: C, 85.67; H, 7.99. Found: C, 85.12; H, 8.12.

Compound 6b was decomposed with HCl in an entirely analogous manner. Yield: Cp_2TiCl_2, 80%; organic product, 100%. Calcd. for organic product: C, 87.96; H, 6.71. Found: C, 87.04; H, 7.24.

Isomer 8 was decomposed in an analogous manner, except that the Et_2O solution of 8 was cooled to -78°C, treated with two equivalents of HCl, and allowed to warm to room temperature. After work-up in air, there was obtained Cp_2TiCl_2 (80%) and the expected organic product (80%). (See Table 3 for data on the organic product.)

Reaction of 6a with CO. Compound 6a (20 mg, 0.047 mmol) was placed in 300 µl THF-d_8 in an NMR tube. The solution was freeze-pump-thawed to remove dissolved gases, placed under 1 atm of CO, and sealed. The reaction was followed by NMR, and was complete in two weeks at 70°C. The orange solution had become pale yellow, and a white precipitate had formed. No evidence for organometallic products could be observed, but an organic product was identified as the acid formed from CO insertion based on its NMR, IR and mass spectra (see Table 4 in text). The

source of H_2O (or its equivalent) is unknown. Yield: 78% per Ti.

The reaction was repeated in C_6D_6, but was so slow that no products could be observed in several weeks at 70°C.

Reactions of 3a With Carbonyl Compounds. The reactions of 3a with various carbonyl compounds (see Table 5 in text) were all run in the same manner. Compound 3a (20 mg, 0.072 mmol) was placed in an NMR tube with 300 µl C_6D_6 and anisole or dimethoxyethane as internal standard. One equivalent of carbonyl compound was added via syringe, and the tube was immediately cooled in liquid nitrogen and sealed. Reactions were allowed to proceed at room temperature, with monitoring by NMR. When all 3a had disappeared, the yield of product was measured by NMR or by gas chromatography (Duropak or Carbowax columns). Products of methylene for oxygen exchange were identified by comparison to authentic samples. 3,3-Dimethyl-1-butene was also produced in quantitative yields (by NMR). No organometallic products were visible in the NMR, but a yellow precipitate formed, which matched the literature description of titanocene oxide polymer.[17]

Reactions with aldehydes did not proceed to completion with the addition of only one equivalent of carbonyl substrate; two equivalents were required. One equivalent

of aldehyde presumably is taken up by the titanocene oxide, as it can be accounted for in no other way. The rate of disappearance of 3a in the presence of aldehyde is, however, first order (vide infra).

An entirely analogous approach was used in the experiments with N-benzylidenemethylamine.

Kinetic Data. General. All kinetic data were obtained in the following way: 3a was placed in an NMR tube, which had been marked to indicate a volume of 300 μl. One of two methods was used: either 3a was weighed directly into the tube in the dry box (judged to be accurate to ± 1 mg), or a stock solution of known concentration of 3a in solvent (C_6D_6) was syringed into the tube. There was no particular advantage to either method, except that a stock solution of 3a in C_6D_6 could not, of course, be employed in cases where the reaction was to be run in neat acetone-d_6. (Stock solutions of acetone-d_6 were not employed because the solvent reacts with 3a.) Anisole or dimethoxyethane was used as internal standard (chosen so that their NMR resonances would not interfere with the observation of any other peaks), and was either syringed into each individual tube or included in the stock solution. Any other "inert" materials, such as added alkene 13, were added *via* syringe to the tube. All tubes

were capped with septa when not being manipulated. Finally, carbonyl substrate was added to each tube (measured *via* syringe), the total volume was brought up to 300 μl with C_6D_6, and the tube was closed, removed from the dry box, cooled in liquid nitrogen, and sealed. Care was taken to work quickly once any reactive agent had been added to the tube, and all tubes were frozen in liquid nitrogen within 5 min of any such addition. Tubes were stored at or below -55°C until kinetics could be measured on them.

For each set of kinetic data, a t=0 spectrum was measured upon first thawing the tubes, and tubes were then placed in a constant temperature bath, sealed end down. The amount of 3a present at various points in the time was measured by NMR, integrating one of the Cp resonances of 3a and the internal standard. The NMR probe was maintained at 34°C, and samples were centrifuged at ambient temperature prior to insertion in the NMR probe, but the total amount of time necessary to accomplish the centrifugation and NMR measurement was less than 4 min, and this was judged to be a negligible amount of time for a sample to be out of the temperature bath. Since solid titanocene oxide polymer precipitates out of the reaction in most cases, it was necessary to allow the reactions to proceed in the

sealed end of the NMR tube and to centrifuge each sample prior to NMR measurement, so that solids would not interfere with the resolution of the NMR spectrum.

The data were worked up as follows:

Let A = the area of the Cp peak of 3a at time t

A_o = the area at time t=0

S = the area of the internal standard at time t

S_o = the area of the internal standard in the t=0 spectrum

A plot was made of $-\ln(AS_o/A_oS)$ versus time t. The slope of this line is the first-order rate constant k_{obs}. Slopes were determined using a linear regression program on a Hewlett-Packard 25 Pocket Calculator, and were checked by graphing the results to see that the calculated results were reasonable and free of obvious errors (i.e., obviously spurious points).

Particular procedures for each kinetics experiment are discussed below.

Determination of Reaction Order. The first kinetics experiments were plotted using both first and second order treatments, for a variety of substrates. The first order calculation has been described above, and the second

order calculation is:

Let A, A_o, S, and S_o be as previously defined.

B = area of substrate at time t

B_o = area of substrate at time t=0

The area of the substrate B was measured directly if possible; otherwise it was calculated, using the amount of 3a remaining and the known stoichiometry of the reaction. Then a plot of $-\ln(AB_o/A_oB)$ versus time yields a line with slope ([3a] - [substrate])k where k is the second order rate constant. (When an aldehyde is the substrate, one must use the value for equivalents of aldehyde rather than the concentration. When equal amounts of 3a and substrate are present, one must plot $(A_o-A)/(A_oA)$ versus time to obtain a slope equal to the rate constant k.) While the first order plots yielded good straight lines and reasonably consistent values for the rate constant, the second order plots gave slightly curving lines and rate "constants" that varied by a factor of 4 or more. The reaction order was concluded to be first order in 3a, zero order in substrate.

Determination of Alkene Dependence. The dependence of the rate of disappearance of 3a on the concentration

of alkene 13 was determined as follows. At least 5 equivalents of 13 and methyl benzoate as carbonyl substrate were placed in each NMR tube with 3a; the high concentrations assured that the concentration of 13 and MB would remain approximately constant over the first half-life of the reaction. The amounts and relative ratios of 13 and MB varied from sample to sample, however (from 1.21 to 3.63 M, and ratios of 2.0 to 0.5). The disappearance of 3a was followed, and plotted using first order kinetics. The data so obtained, and the treatment of them, are described in Table 7 and in the text.

Determination of k_1 by varying [acetone]. At least 10 equivalents of acetone were placed in NMR tubes with 3a; the high concentrations assured an approximately constant concentration of acetone over the first half-life of the reaction. The acetone concentration varied from 2.42 to 13.7 M in different tubes. The disappearance of 3a was monitored, and a first order rate constant k_{obs} obtained for each sample. The data are presented in Table 8 and a treatment of them discussed in the text.

A similar experiment was done using large amounts of acetone and added alkene 13. Within experimental error, no effect of added alkene could be observed with acetone as the carbonyl substrate.

Dependence of k_{obs} on Temperature. It had been determined by the acetone concentration dependence experiments that k_{obs} in neat acetone-d_6 is within 3% of k_1 (see text). It was therefore a simple matter to observe the rate of disappearance of 3a in neat acetone-d_6 at various temperatures (from 4.8 to 51.0°C) and thereby determine E_a and $\Delta S^{\ddagger}$ for the reaction. The results of these experiments are contained in Table 9, and discussed in the text.

Competition Experiments. Mixtures were prepared which were equimolar in each of two competing substrates (acetone and methyl benzoate, acetone and acetophenone, methyl benzoate and ethyl acetate), and these were added to 3a in large enough amounts that the concentration of the two substrates would not vary over the course of the reaction. For example, acetone (580 mg) and acetophenone (1200 mg) were mixed together. 300 µl of this solution (approximately 1.5 mmol of each substrate) was added to 3a (20 mg, 0.072 mmol) in an NMR tube. The tube was sealed, and when the reaction was complete (3 days) the tube was broken open and the product ratios determined by gas chromatography. To determine the effect of added alkene, 300 µl of the acetone/acetophenone mixture was added to a tube containing 3a (20 mg) and 13 (150 µl,

1.2 mmol), and the products again analyzed by gas chromatography.

Competition experiments with 1 were performed by adding an equimolar mixture of pyridine and two competing substrates to 1. For example, pyridine (316 mg) and the acetone/acetophenone mixture described above (710 mg) were mixed, cooled to -40°C, and the mixture then added to an NMR tube at -40°C containing 1 (20 mg, 0.07 mmol). The reaction tube was immediately cooled in liquid nitrogen, and sealed. Upon warming to room temperature, reaction was complete. Product ratios were determined by gas chromatography.

Photochemical Reaction of 3a with Acetone. 3a (20 mg) was placed in 300 µl acetone-d_6 in a Pyrex NMR tube, with dimethoxyethane as internal standard. The tube was irradiated with an unmodified UV light (Hanovia 579A36 High Pressure Hg Light Source) at -20°C, and the first order rate of disappearance of 3a was followed by NMR and determined to be 3.1×10^{-5} sec^{-1}. The calculated rate of the thermal reaction at this temperature is 3.5×10^{-8} sec^{-1}. At higher temperatures, the thermal reaction began to be competitive with the photochemical one, so that the overall rate of disappearance of 3a with or without irradiation at ambient temperatures was nearly the same.

References and Notes

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(8) Pine, S. H.; Howard, T. R. Unpublished results. This material is probably formed from titanocene oxide or some other titanocene product and Me_2AlCl. Aluminum oxides are also formed.

(9) Tebbe, F. N. Private communication.

(10) No neopentane was observed in gas chromatographic analyses, but this is undoubtedly due to variations in reaction conditions, length of reaction, etc., to

which the system is quite sensitive.

(11) Identified by comparison of NMR spectrum and melting point to published data: Waters, J. A.; Mortimer, G. A. J. Organomet. Chem. 1970, 22, 417. The material also showed a positive Cl test (green flame).

(12) Howard, T. R. Unpublished results.

(13) Compound 3d was prepared from 1 and 2-butyne in the presence of 2-vinylpyridine-styrene copolymer, as described for the preparation of the metallacyclobutanes in Reference 5. Complete data are included in the Experimental Section.

(14) They can even be chromatographed on alumina on a bench-top. They appear to be slightly unstable in benzene solution in air, but are not at all sensitive in diethyl ether or CCl_4 solutions.

(15) Nesmeyanov, A. H.; Nogina, O.; Berlin, A.; Girshovich, A.; Shatalov, G. V. Bull. Acad. Sci. USSR, Div. Chem. Sci. 1961, 2008.

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(17) Giddings, S. A. Inorg. Chem. 1964, 3, 684.

(18) A crystal structure of 3a is in progress; Grubbs,

R. H.; Schaeffer, W. A.; Howard, T. R.

(19) The data for several different substrates at several different concentrations were plotted using both first and second order treatments. A much better fit was obtained for the first order plots; in addition, the second order rate constant so obtained varied by huge amounts.

(20) Titanocene oxide polymer precipitates out of most solvents and appears as a broad lump at δ 6.0 to 7.0 in the NMR when it does remain in solution. When aldehyde is the substrate, one equivalent of aldehyde appears as alkene product and the other is evidently incorporated into the insoluble organometallic polymer, as it appears nowhere else.

(21) Rates of reaction of ketones and esters with $\underset{\sim}{1}$ vary greatly, ketones being several orders of magnitude faster: Pine, S. H. Unpublished results.

(22) This assumes (a) that pyridine will react with $\underset{\sim}{1}$ faster than acetone or methyl benzoate will, and (b) that the pyridine·$AlMe_2Cl$ complex is entirely removed from the coordination sphere of the titanium, thus generating $\underset{\sim\sim}{12}$.

(23) Since k_3 and k_4 will be different for different substrates, we have designated k_3 and k_4 to represent

the rates of reaction of 11 and 12, respectively, with methyl benzoate, and k_3, and k_4, to refer to the analogous reactions with acetone.

(24) Note that this value is only 3% different than the k_{obs} obtained in neat acetone-d_6.

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APPENDIX I

Derivation of Kinetic Expressions

A. For Scheme V, Case 1 (see text):

$$\underset{\sim\sim}{3a} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\sim\sim}{11} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\sim\sim}{12} + \underset{\sim\sim}{13}$$

$$\underset{\sim\sim}{12} \xrightarrow{k_4[C]} \text{products}$$

C = carbonyl substrate

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_1[\underset{\sim\sim}{3a}] - k_{-1}[\underset{\sim\sim}{11}] \qquad (1)$$

Using a steady-state approximation,

$$\frac{d[\underset{\sim\sim}{11}]}{dt} = 0 = k_1[\underset{\sim\sim}{3a}] - k_{-1}[\underset{\sim\sim}{11}] - k_2[\underset{\sim\sim}{11}] + k_{-2}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}] \qquad (2)$$

$$[\underset{\sim\sim}{11}] = \frac{k_1[\underset{\sim\sim}{3a}] + k_{-2}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}]}{k_{-1} + k_2} \qquad (3)$$

$$\frac{d[\underset{\sim\sim}{12}]}{dt} = 0 = k_2[\underset{\sim\sim}{11}] - k_{-2}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}] - k_4[\underset{\sim\sim}{12}][C] \qquad (4)$$

$$[\underset{\sim\sim}{12}] = \frac{k_2[\underset{\sim\sim}{11}]}{k_{-2}[\underset{\sim\sim}{13}] + k_4[C]} \qquad (5)$$

Substituting for $[\underset{\sim\sim}{12}]$ in Equation (3) and simplifying, one obtains:

$$[\underset{\sim\sim}{11}] = \frac{k_1[\underset{\sim\sim}{3a}](k_{-2}[\underset{\sim\sim}{13}] + k_4[C])}{k_{-1}(k_{-2}[\underset{\sim\sim}{13}] + k_4[C]) + k_2k_4[C]} \quad (6)$$

Substituting for $[\underset{\sim\sim}{11}]$ in Equation (1) and simplifying gives:

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_1[\underset{\sim\sim}{3a}] \left\{ \frac{k_2k_4[C]}{k_{-1}(k_{-2}[\underset{\sim\sim}{13}] + k_4[C]) + k_2k_4[C]} \right\} \quad (7)$$

If $[\underset{\sim\sim}{13}]$ and [C] are large enough relative to $[\underset{\sim\sim}{3a}]$ that they do not vary with time, then:

$$k_{obs} = k_1 \left\{ \frac{k_2k_4[C]}{k_{-1}(k_{-2}[\underset{\sim\sim}{13}] + k_4[C]) + k_2k_4[C]} \right\} \quad (8)$$

or

$$\frac{k_1}{k_{obs}} = \left(1 + \frac{k_{-1}}{k_2}\right) + \left\{\frac{k_{-1}k_{-2}}{k_2k_4}\right\} \frac{[\underset{\sim\sim}{13}]}{[C]} \quad (9)$$

B. For Scheme V, Case 2, including the equilibrium between $\underset{\sim\sim}{12}$ and $\underset{\sim\sim}{13}$ (see text):

$$\underset{\sim\sim}{3a} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\sim\sim}{11} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{\sim\sim}{12} + \underset{\sim\sim}{13}$$

$$\underset{\sim\sim}{11} \xrightarrow{k_3[C]} \text{products}$$

C = carbonyl substrate

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_1[\underset{\sim\sim}{3a}] - k_{-1}[\underset{\sim\sim}{11}] \qquad (1)$$

Using a steady-state approximation,

$$\frac{d[\underset{\sim\sim}{11}]}{dt} = 0 = k_1[\underset{\sim\sim}{3a}] - k_{-1}[\underset{\sim\sim}{11}] - k_2[\underset{\sim\sim}{11}] + k_{-2}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}] - k_3[\underset{\sim\sim}{11}] \qquad (2)$$

$$[\underset{\sim\sim}{11}] = \frac{k_1[\underset{\sim\sim}{3a}] + k_{-2}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}]}{k_{-1} + k_2 + k_3[C]} \qquad (3)$$

$$\frac{d[\underset{\sim\sim}{12}]}{dt} = 0 = k_2[\underset{\sim\sim}{11}] - k_{-2}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}] \qquad (4)$$

$$[\underset{\sim\sim}{12}] = \frac{k_2[\underset{\sim\sim}{11}]}{k_{-2}[\underset{\sim\sim}{13}]} \qquad (5)$$

Substituting for $[\underset{\sim\sim}{12}]$ in Equation (3) and simplifying, one obtains:

$$[\underset{\sim\sim}{11}] = \frac{k_1[\underset{\sim\sim}{3a}]}{k_{-1} + k_3[C]} \qquad (6)$$

Note that this is the same expression one would obtain if one ignored the equilibrium between $\underset{\sim\sim}{11}$ and $\underset{\sim\sim}{12}$, and derived an expression for $[\underset{\sim\sim}{11}]$ based on a steady-state of $\underset{\sim\sim}{11}$. Substituting for $[\underset{\sim\sim}{11}]$ in Equation (1) and simplifying gives:

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_1[\underset{\sim\sim}{3a}] \left(\frac{k_3[C]}{k_{-1} + k_3[C]} \right) \qquad (7)$$

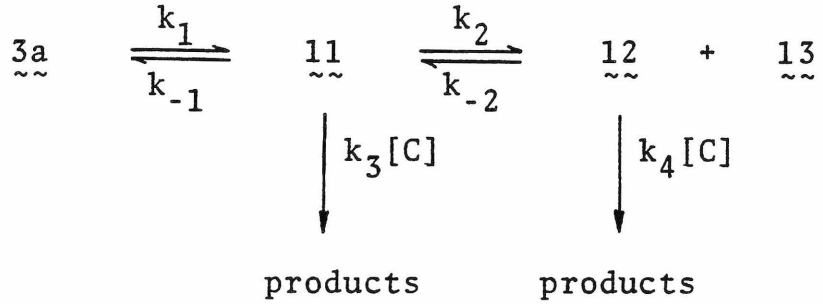
If [C] is large enough relative to $[\underset{\sim\sim}{3a}]$ so that it does not vary with time, then

$$k_{obs} = \frac{k_1 k_3[C]}{k_{-1} + k_3[C]} \qquad (8)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \left(\frac{k_{-1}}{k_1 k_3} \right) \left(\frac{1}{[C]} \right) \qquad (9)$$

C. For Scheme V, Case 3 (see text):



C = carbonyl substrate

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_1[\underset{\sim\sim}{3a}] - k_{-1}[\underset{\sim\sim}{11}] \qquad (1)$$

Using a steady-state approximation for $\underset{\sim\sim}{11}$ and simplifying gives:

$$[\underset{\sim\sim}{11}] = \frac{k_1[\underset{\sim\sim}{3a}] + k_{-2}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}]}{k_{-1} + k_2 + k_3[C]} \qquad (2)$$

Using a steady-state approximation for $\underset{\sim\sim}{12}$ and simplifying gives:

$$[\underset{\sim\sim}{12}] = \frac{k_2[\underset{\sim\sim}{11}]}{k_{-2}[\underset{\sim\sim}{13}] + k_4[C]} \qquad (3)$$

Substituting this value back into Equation (2) gives:

$$[\underset{\sim\sim}{11}] = \frac{k_1[\underset{\sim\sim}{3a}](k_{-2}[\underset{\sim\sim}{13}] + k_4[C])}{(k_{-2}[\underset{\sim\sim}{13}] + k_4[C])(k_{-1} + k_3[C]) + k_2k_4[C]} \qquad (4)$$

Substituting for $[\underset{\sim\sim}{11}]$ in Equation (10 and simplifying gives:

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_1[\underset{\sim\sim}{3a}]\left\{\frac{k_3[C](k_{-2}[\underset{\sim\sim}{13}] + k_4[C]) + k_2k_4[C]}{(k_{-1} + k_3[C])(k_{-2}[\underset{\sim\sim}{13}] + k_4[C]) + k_2k_4[C]}\right\} \tag{5}$$

If $[\underset{\sim\sim}{13}]$ and [C] are large enough relative to $\underset{\sim\sim}{3a}$ that they do not vary with time, then:

$$k_{obs} = k_1\left\{\frac{k_3[C](k_{-2}[\underset{\sim\sim}{13}] + k_4[C]) + k_2k_4[C]}{(k_{-1} + k_3[C])(k_{-2}[\underset{\sim\sim}{13}] + k_4[C]) + k_2k_4[C]}\right\} \tag{6}$$

or

$$\left(\frac{k_1}{k_{obs}} - 1\right)^{-1} = \frac{k_2k_4[C]}{k_{-1}(k_{-2}[\underset{\sim\sim}{13}] + k_4[C])} + \frac{k_3[C]}{k_{-1}} \tag{7}$$

For substrates such as acetone, for which $k_4[C] >> k_{-2}[\underset{\sim\sim}{13}]$, this simplifies to:

$$\left(\frac{k_1}{k_{obs}} - 1\right)^{-1} = \frac{k_2}{k_{-1}} + \frac{k_3}{k_{-1}}[C] \tag{8}$$

D. For Scheme V, Case 4 (see text):

$$\underset{\sim\sim}{3a} \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} \underset{\sim\sim}{12} + \underset{\sim\sim}{13}$$

$$\Big\downarrow k_4[C]$$

products

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_5[\underset{\sim\sim}{3a}] - k_{-5}[\underset{\sim\sim}{12}][\underset{\sim\sim}{13}] \qquad (1)$$

Using a steady-state approximation for $\underset{\sim\sim}{12}$ and simplifying gives:

$$[\underset{\sim\sim}{12}] = \frac{k_5[\underset{\sim\sim}{3a}]}{k_{-5}[\underset{\sim\sim}{13}] + k_4[C]} \qquad (2)$$

Substituting this expression back into Equation (1) and simplifying yields:

$$\frac{-d[\underset{\sim\sim}{3a}]}{dt} = k_5[\underset{\sim\sim}{3a}] \left\{ \frac{k_4[C]}{k_{-5}[\underset{\sim\sim}{13}] + k_4[C]} \right\} \qquad (3)$$

If $[\underset{\sim\sim}{13}]$ and [C] are large enough relative to $\underset{\sim\sim}{3a}$ so that they do not vary with time, then:

$$k_{obs} = \frac{k_5 k_4[C]}{k_{-5}[\underset{\sim\sim}{13}] + k_4[C]} \qquad (4)$$

or

$$\frac{1}{k_{obs}} = \frac{1}{k_5} + \frac{k_{-5}[13]}{k_5 k_4 [C]} \qquad (5)$$

CHAPTER II:

SYNTHESIS OF AND REDUCTIVE ELIMINATION FROM PLATINUM-VINYL COMPOUNDS

INTRODUCTION

The examination of reductive elimination from transition metal complexes (Reaction 1) has received a great deal

$$M(R)(R') \rightarrow M + R{-}R' \qquad (1)$$

of attention. Studies have been done with a variety of organic fragments R and R'; for example, the systems described in Table I are representative of the work on platinum systems alone (which are admittedly studied more extensively than many other metal systems, although work

Table I
Reductive Elimination from Pt Systems

R	R'	Reference # (metal)
Me	Me	1(Pt IV), 2(Pt IV)
n-Bu	n-Bu	3(Pt II)
Me	H	4(Pt II)
aryl	aryl	5(Pt II)
Me	CH_3C O	6(Pt IV)
metallacycles		7(Pt II), 8(Pt II), 9(Pt IV)

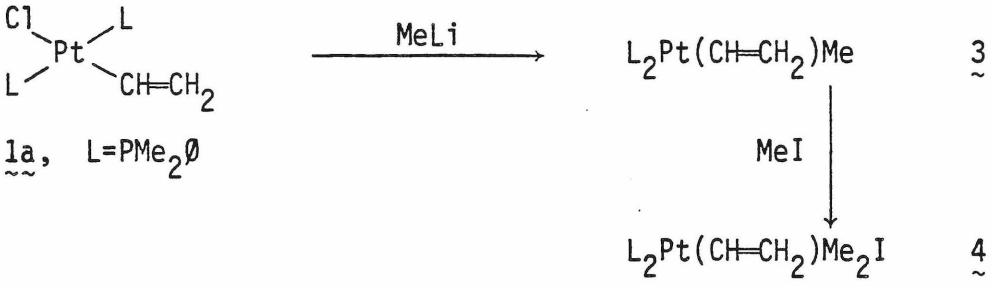
has also been done with Zr,[10,11] Ta,[12] Mo,[13] Os,[14] Co,[15] Ni[16-18] and Au[19,20]). In spite of this tremendous amount of research, reductive elimination involving vinyl ligands has not been examined, and, in fact, relatively few vinyl compounds are known. Some of the best-characterized vinyl compounds are those of platinum, $L_2Pt(CH{=}CH_2)X$, L = $PMe_2\emptyset$ or $PEt_2\emptyset$, X = Cl, Br, I.[21] There is also evidence of reductive elimination

of propene from $(PEt_2\emptyset)_2PtMe(CH{=}CH_2)I_2$.[22] Furthermore, as is obvious from Table I, reductive elimination from a great many platinum II and IV systems is already well studied. Therefore, it seemed reasonable to undertake a study of the reductive elimination reactions of platinum II and IV vinyl compounds.

RESULTS AND DISCUSSION

Syntheses of Platinum-Vinyl Compounds

Syntheses of $L_2Pt(CH{=}CH_2)X$ 1 have been reported, and one can make $L_2Pt(CH{=}CH_2)Me(I)X$ 2 via the oxidative addition of MeI to the Pt(II) compounds. The synthesis of 2 takes approximately four weeks at room temperature, however, and cannot be greatly accelerated by heating without the occurrence of reductive elimination to form $L_2Pt(I)X$.[22] Platinum chlorides are substituted easily with MeLi or MeMgBr in a number of cases, so that one might expect to be able to make $L_2Pt(CH{=}CH_2)Me$.[23,24] Oxidative addition to Pt(II) dialkyls appears to proceed much more rapidly than to Pt(II) alkyl halides.[24,25] With these facts in mind, the following synthetic scheme was planned:



1a, L=$PMe_2\emptyset$

Scheme I

Treatment of 1a with MeLi at -78°C does, indeed, afford 3 in 87% isolated yield. IR and ^1H NMR spectra of 3 are shown in Figure I, and the ^1H and ^{31}P NMR data are listed in Table II. The fact that two different phosphine resonances (J_{P-P} = 14 Hz) are observed by ^{31}P NMR identifies 3 as the cis isomer, a structure which is also consistent with the coupling constants J_{Pt-P} and J_{Pt-H}. The NMR assignments are based on the assumption that the chemical shift and coupling constants of the $PMe_2\emptyset$ ligand trans to $-CH_3$ will be more similar to the ligands in cis-$(PMe_2\emptyset)_2PtMe_2$ 5 than the ligand trans to $-CH{=}CH_2$. The ^{31}P NMR spectral data for 5 are included in Table II for reference. The IR spectrum of 3 shows a C=C stretch at 1557 cm^{-1}. This may be compared to a C=C stretch at 1564 cm^{-1} in 1a.[22]

Care must be taken in the synthesis of 3 to avoid the formation of 5.[26] An excess of MeLi, fast addition rates or a higher reaction temperature will result in a final product containing up to 20% 5. Use of MeMgI (instead of MeLi) or excess 1a will not prevent the formation of 5; the alternate synthetic approach in Reaction (2) is unsuccessful as no reaction at all occurs. Furthermore,

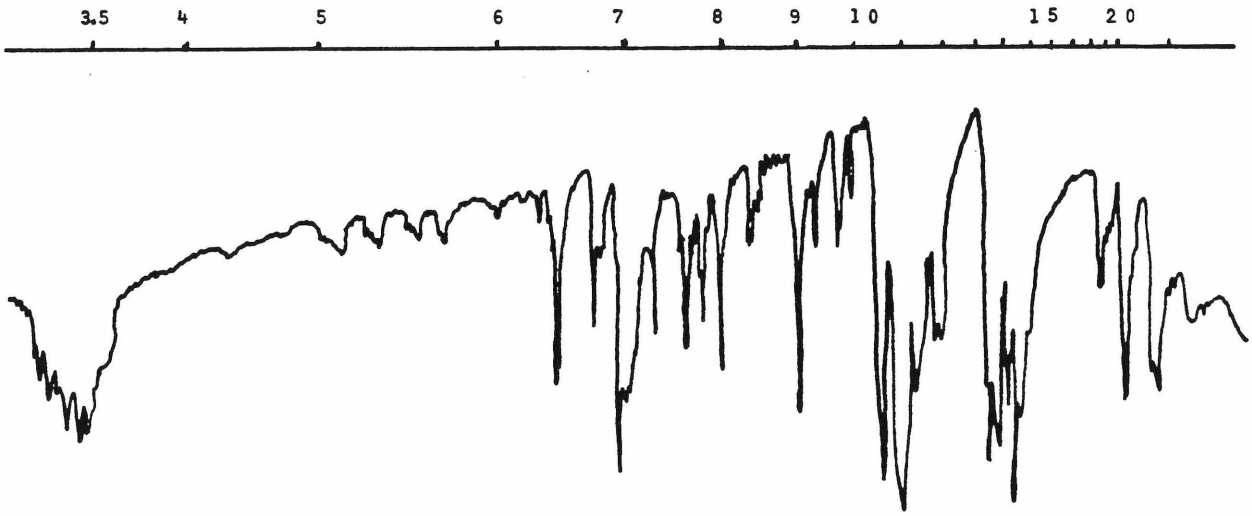
$$1a + R_3Sn(CH{=}CH_2) \xrightarrow{?} 3 \qquad (2)$$

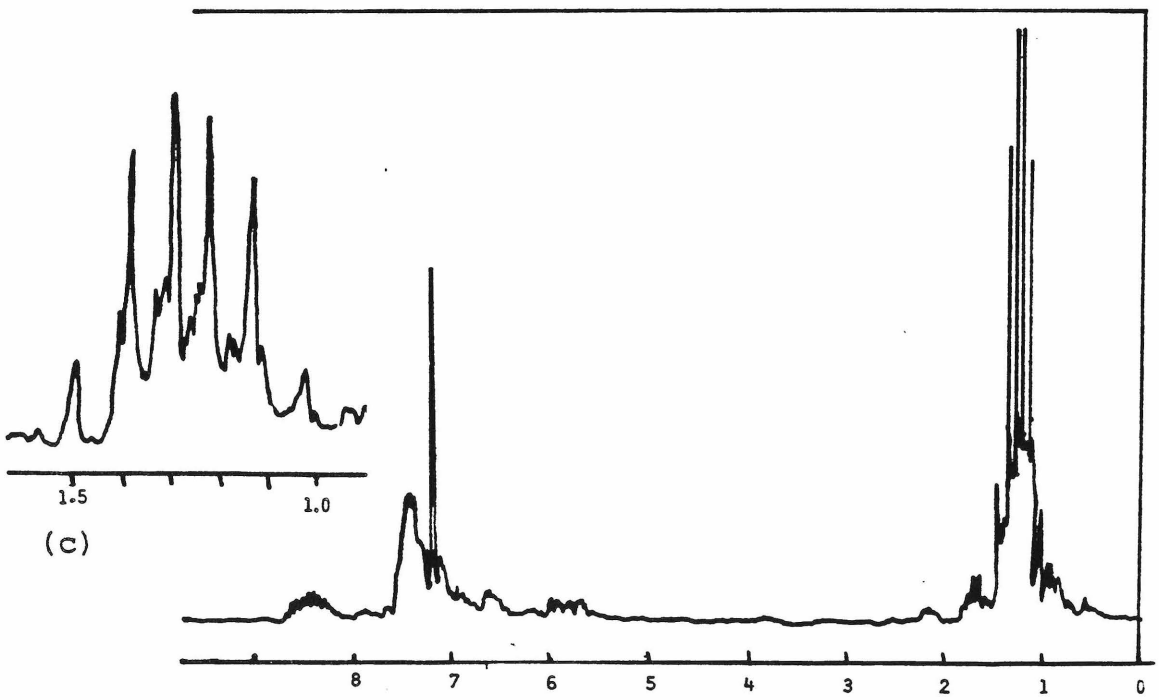
separation of 3 and 5 is difficult by recrystallization or column chromatography. The presence of 5 is not evident on the basis of melting point (3 containing 20% 5 melts at 70.5 - 71.5°C, and the expected lowered broadened melting point is only observed in nearly 50:50 mixtures) nor is it easily distinguishable by ^1H NMR. ^{31}P NMR, however, readily distinguishes the two, and the IR spectra between 1150 and 1250 cm^{-1} also

Figure I

IR and ^1H NMR Spectra for 3

a IR(KBr)



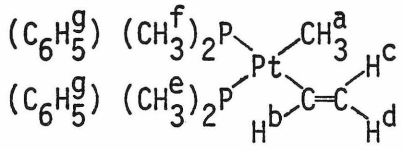
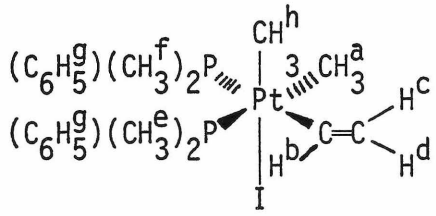


c. Expansion (5x) of region between δ1.0 and 1.5.

b. NMR(C_6D_6)

Table II

NMR Data

Compound	^{1}H Spectrum in C_6D_6		
	assignment: δ	J_{P-H}(Hz)	J_{Pt-H}(Hz)
	a: 1.30(3H),mult[a,b,c]	9.5 7.1	69
	b: 8.40(1H),mult		
	c: 5.82(1H),mult		
3	d: 6.61(1H),mult[d]		
	e: 1.33(6H),doub[b]	7.8	21.0
	f: 1.17(6H),doub[b]	7.7	18.6
	g: 7.03(6H),mult 7.41(4H),mult		
	a,e,f: 1.15 to 1.8 (15H),mult[e]		
	b: 8.06(1H),mult, J_{bc} = 12 Hz		
	c: 5.84(1H),mult, J_{cd} = 2 to 3 Hz		
4	d: 7.36(1H),mult, J_{bd} = 9 Hz, $J_{P-H}{}^{d}$ = 18 Hz		
	g: 7.15(6H),mult 7.21(4H),mult		
	h: 0.84(3H),trip[b]	7.5	67

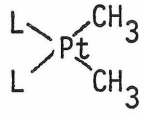
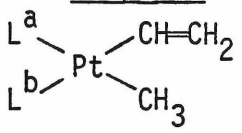
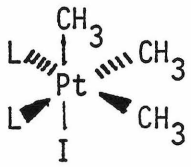
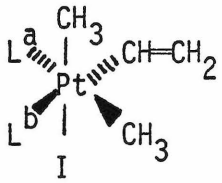
Compound	^{31}P Spectrum in C_6D_6, Proton Decoupled
L=$PMe_2Ø$	Position in ppm relative to H_3PO_4(J_{Pt-P},Hz)
 5	-12.1(1824)

Table II (continued)

Compound		^{31}P Spectrum in C_6D_6, Proton Decoupled
	3	a: -13.6(1821) J_{P-P} = 14 Hz b: -14.4(1724)
	6	-47.0(1164)
	4	a: -47.4(1174) b: -47.4(1152)

a. Non-first-order four line pattern.

b. Multiplet due to phosphorous couplings is further split into a doublet due to coupling to ^{195}Pt, which is present in approximately 30% abundance.

c. Only the resonances coupled to Pt are clearly visible; the central, non-Pt-coupled resonance is obscured by other peaks. The position of the central resonance is inferred from the positions of the Pt-coupled peaks.

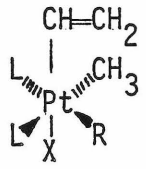
d. Tentative assignment.

e. The spectrum is too complex to permit definite assignments for each methyl group.

allow one to see relatively small amounts of 5 in 3 (Figure II).

Dissolution of 3 in MeI followed by standing for approximately one week at room temperature or 20 hours at 40°C results in oxidative addition of MeI to the Pt(II) compound. IR and ^{1}H NMR spectra for 4 are shown in Figure III, and the ^{1}H and ^{31}P NMR data are listed in Table II. The ^{31}P NMR spectrum shows coincidentally identical chemical shifts for the two $PMe_2\emptyset$ ligands, but different J_{Pt-P}'s, indicating inequivalent phosphorus atoms. Both coupling constants (J_{Pt-P} = 1152, 1174 Hz) are too small to indicate an iodine trans to a phosphorus (such coupling constants are generally in the range of 3500 to 4500 Hz[22,27,28]). Thus, the structure of 4 is as shown in Table II. The ^{1}H NMR spectrum is too complex to permit the assignment of all resonances and coupling constants, but J_{Pt-H} for $-CH_3^h$ is consistent with the assignment. The IR spectrum shows a C=C stretch at 1578 cm^{-1}.

Attempts to generate 4 or another isomer, possibly 7a, or a



L = $PMe_2\emptyset$
7a: R = Me
7b: R = CH=CH_2

Pt(IV)divinyl complex (such as 7b) via oxidative addition of vinyl halide to Pt(II) (3 or 5) were unsuccessful. Reaction of 3 or 5 with $BrCH{=}CH_2$ is much slower than the reaction with MeI (in reaction times comparable to those used to make 4, large amounts of unchanged starting material remained). However, even in low percentage conversion reactions, no Pt(IV) product is observed (by ^{31}P NMR), and the species observed

Figure II

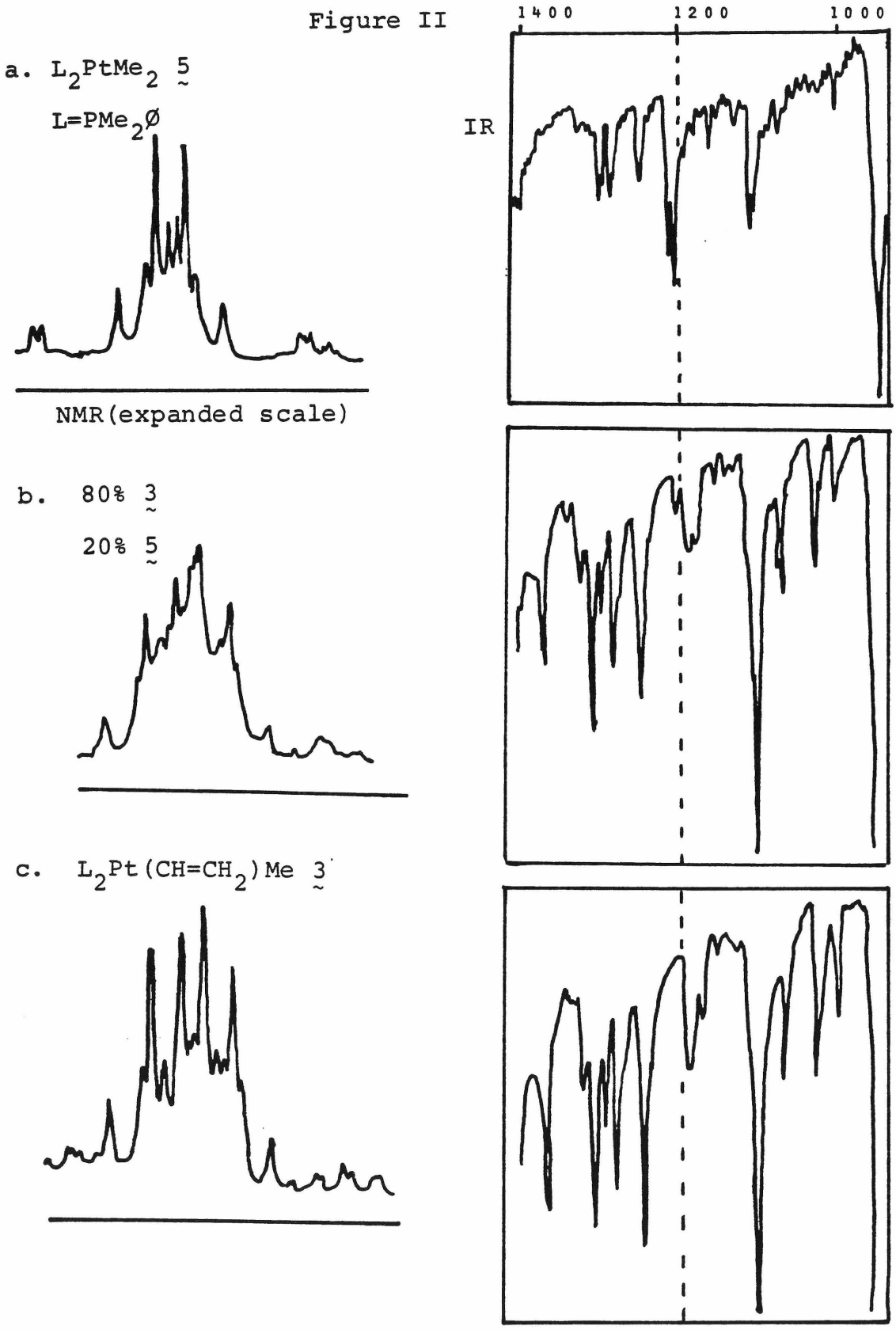
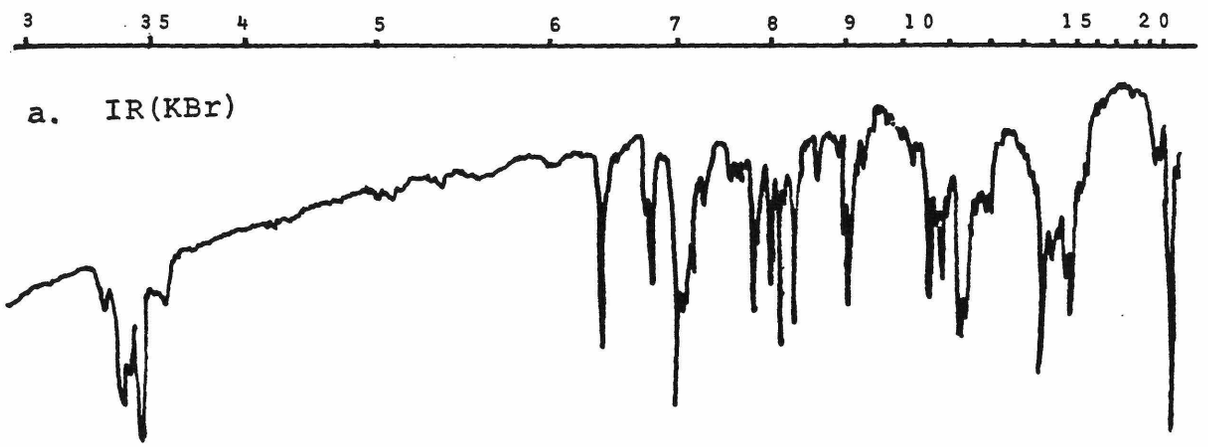
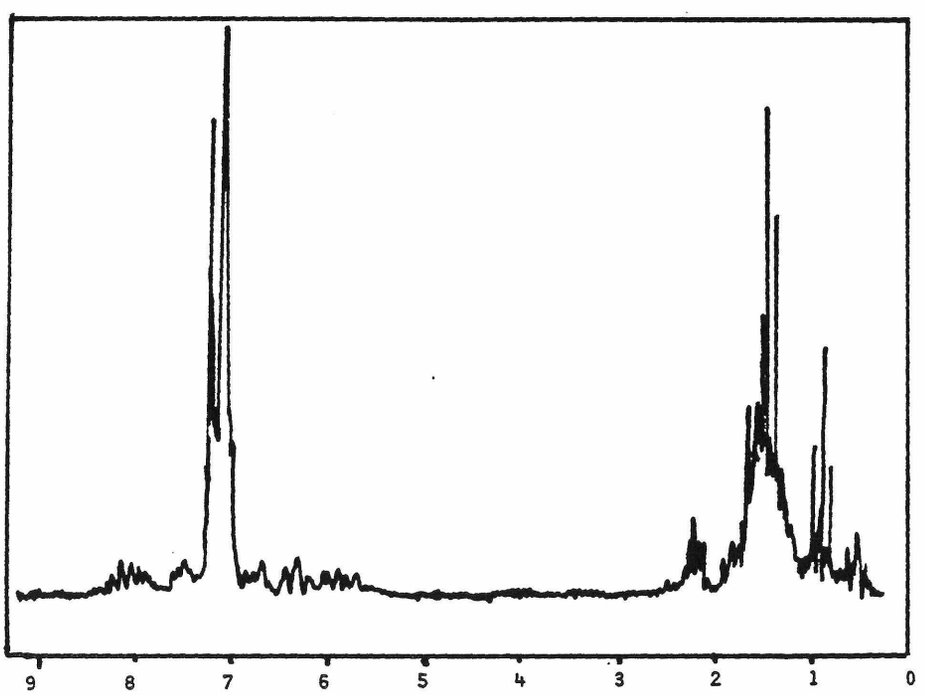

1400
1200
1000
a. L_2PtMe_2 5
L=$PMe_2Ø$
IR
NMR(expanded scale)
b. 80% 3
20% 5
c. $L_2Pt(CH=CH_2)Me$ 3

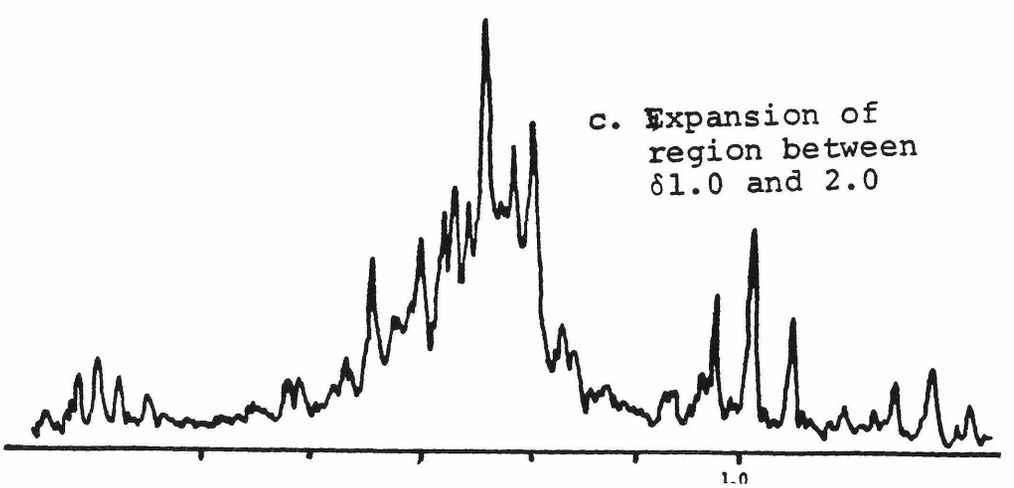
Figure III: IR and ^{1}H NMR Spectra for 4



a. IR(KBr)



b. NMR(C_6D_6)



c. Expansion of region between δ1.0 and 2.0

generally correspond to the expected Pt(II) products of reductive elimination from 7. IR spectra show no evidence of new vinyl C=C stretches. Gas chromatographic analysis of the organic products of thermal decomposition of what was expected to be 7 (after work-up)[29] showed small amounts of the products expected from reductive elimination of 7, but much larger amounts of the products expected from thermal decomposition of Pt(II) species (see Table IV).[29]

The failure to observe any Pt(IV) species with a vinyl group trans to halogen, in addition to the observation of the expected products of reductive elimination from such a species, suggests that the rate of decomposition (reductive elimination or other decomposition pathways) of 7 (or similar molecules) is equal to or greater than the rate of its formation. Other possibilities (secondary reactions or variations in the mechanism of oxidative addition of vinyl halides) have not, however, been ruled out.[30]

Thermal Decomposition of Platinum Compounds

Thermal decomposition of 3 and 4 was accomplished by heating solid samples and/or benzene solutions of the compounds. Gases evolved were analyzed by gas chromatography, and some organometallic products were identified by NMR. Results of the studies are summarized in Table III.

Thermal decompositions of 5 and 6 were also examined briefly for comparative purposes.

Decomposition of 3 produces CH_4 and $CH_2{=}CH_2$ in a ratio of about 1:2, as well as small amounts of the reductive elimination product propene. The major products may arise from a Pt(IV) hydride formed by oxidative

Table III

Thermal Decomposition of Platinum Compounds

Compound	Decomposition Method	Products					
		Gas Chromatographic Analysis (%)				^{31}P NMR[b]	^{1}H NMR[c]
		CH_4	C_2H_4	C_2H_6	propene[a]		
3	Melt (140°C)	32.4	61.2	0	5.5		
4	Melt (155°C)	1.3	0.3	52.7	45.7		
	Soln (90°C)	0.4	0	2.4	97.2	trans-L_2PtMeI	
5	Melt (100°C)	96	2	1	0		
6[d]	Melt (160°C)	3	0	97	0		trans-L_2PtMeI
	Soln (160°C)[e]	12	0	88	0		

a. No evidence of reaction of Pt(II) species with propene was obtained.

b. ^{31}P NMR spectra were taken when appropriate and when instrumentation was available.

c. ^{1}H NMR can be used to identify relatively pure materials, but spectra of complex mixtures cannot be used to reliably identify products.

d. See Ref. 1. Puddephatt et al. report C_2H_6 as the sole organic product.

e. Some CH_4 may be forming from decomposition of L_2PtMeI.

Table IV

Products from the Reaction of Pt(II) and Vinyl Halide

Reactants	Products					
	Gas Charomatographic Analysis after work-up (see Note 29) as % of total organic products.					^{31}P NMR, L = $PMe_2\emptyset$
	CH_4	C_2H_4	C_2H_6	$CH_2{=}CHCH_3$	butadiene	
5 + $BrCH{=}CH_2$	73	1.4	16	9.5	0	cis-L_2PtMe_2(92%) trans-$L_2PtMeBr$ (5%) trans-$L_2Pt(CH{=}CH_2)Br$ (3%)
3 + $BrCH{=}CH_2$	39	33	0	4.5	24	3 (28%) 5 (40%)[a] trans-$L_2PtMeBr$ (19%) trans-$L_2Pt(CH{=}CH_2)Br$ (14%)

a. The source of this product, which is not present in the starting material 3, is unclear. It suggests that simple oxidative addition/reductive elimination is not sufficient to explain these reactions.

addition of Pt(II) into a C–H bond (i.e., ortho-metallation of a phenyl group on $PMe_2\emptyset$ or perhaps insertion into a P–CH_2–H bond), which then eliminates reductively.[7] No acetylene, which might have been produced *via* β-abstraction from the vinyl group, was observed.[31]

The solution decomposition of 4 is first order for disappearance of 4 (followed by ^1H NMR), and indicates that the rate of reductive elimination of vinyl is 20 times faster than that of methyl (after correction for the statistical consideration that there are two ways to make propene and only one way to make ethane). $t_{1/2}$ for the reaction at 83.5°C is 14 min.

Melt decomposition of 4 products approximately equal amounts of ethane and propene. Puddephatt[1] also obtained different results from solution and melt decompositions, although his results would have led one to expect even more propene than is produced in the solution decomposition. He suggests that the two groups *trans* to $PMe_2\emptyset$ leave, and that incomplete scrambling of these two positions and the position *trans* to halogen prior to reductive elimination occurs in melt decomposition. (Complete scrambling occurs in solution decompositions.) If scrambling is incomplete in melt decompositions, then the observation of even greater amounts of ethane suggests that one of the leaving groups is *trans* to halogen. The lability of a vinyl group *trans* to halogen may also explain the failure to observe any products of the type 7a or b in additions of vinyl halide to Pt(II).

Small amounts of CH_4 are produced in all decompositions of Pt(IV) compounds (the large amount of CH_4 in the solution decomposition of 6 may be due to a reaction of L_2PtMeI). Whether the source of the CH_4 is Pt(II)

or Pt(IV) in all cases is unclear, but it certainly constitutes a minor pathway.

The materials produced in attempted syntheses of 7a and b showed no evidence by ^{31}P NMR for Pt(IV) species, and yet subsequent decomposition of these materials showed what appears on the surface to be incorporation of a vinyl group. Considering that small amounts of Pt(IV) species would not have been observed by NMR and that studies of the decomposition modes of $L_2Pt(R)X$ (R = Me, $CH{=}CH_2$) have not been done, this should not be considered inconsistent. Observation of 3 or 4 in neat vinyl halide at varying temperatures by ^{31}P NMR (and subsequent observation of the organics produced by gas chromatography, before work-up) would be certainly informative.[29]

EXPERIMENTAL

General

Spectro-grade benzene, and reagent-grade toluene, THF and diethyl ether were vacuum-transferred from sodium benzophenone ketyl prior to use. Petroleum ether (bp. 35 - 60°C) was washed twice with H_2SO_4, twice with saturated $KMnO_4$ in 10% H_2SO_4, and dried and distilled from sodium benzophenone ketyl. K_2PtCl_4, $PMe_2\emptyset$, $(n\text{-}Bu)_3Sn(CH{=}CH_2)$ and MeLi were used as supplied. MeI and $BrCH{=}CH_2$ were degassed (3 freeze-pump-thaw cycles) prior to use.

Proton NMR spectra were recorded on a Varion Associates EM-309 NMR spectrometer. ^{31}P NMR spectra were recorded on a Bruker WH-90, IR spectra on a Beckman 4240, and UV spectra on a Cary 14. Gas chromatographic analyses were performed on a Varian Aerograph Series 1400 GC, using Porapak Q (8' x 1/8" column, 80/100 mesh commercial Porapak Q, 70°C) for C_1 - C_4 species and Duropak (20' x 1/8", 100/120 mesh, 80°C) for C_2 - C_6 species.

Manipulations requiring an inert atmosphere were performed in a Vacuum Atmospheres Recirculating Dry Box or under purified argon using standard Schlenk Techniques.

Syntheses

The synthesis of $(PMe_2\emptyset)_2PtCl_2$ has been described.[32] The synthesis of 1a from this has also been described,[22] and we have discovered that the use of $(n\text{-}Bu)_3Sn(CH{=}CH_2)$ instead of the described $Me_3Sn(CH{=}CH_2)$

results in improved yields (up to 52%).

$(PMe_2Ø)_2Pt(CH{=}CH_2)Me$, 3: 3 was made by adding MeLi (1.56 M in diethylether, 1.1 ml, 1.7 mmol) dropwise over a period of 45 min. to a solution of 1a in THF (0.92 g, 1.7 mmol in 150 ml) in a 250 ml round-bottom flask stirred magnetically, at -78°C under an inert atmosphere. The reaction mixture was stirred for an additional 2 hrs. while it warmed to -50°C. At -50°C, 3 ml MeOH was added to destroy any remaining MeLi. Work-up was continued at ambient temperature, in air: the solvents were removed with the use of a rotary evaporator, water was added to the solids, and the suspension that formed was extracted with three portions of ether. The combined ether extracts were dried over $MgSO_4$ (anhydrous), the solvent was removed, and the resulting solids recrystallized from toluene/petroleum ether at -40°C in the dry box. Obtained: 0.77 g 3 (87% yield), mp. 70.5 - 71.5°C. Calc: C 44.44, H 5.5%, found: C 44.35, H 5.44%. UV(MeOH): shoulder at 310 nm on a peak which continues to increase until the solvent cut-off.

$(PMe_2Ø)_2Pt(CH{=}CH_2)Me_2I$, 4: 4 was prepared by dissolving 3 (300 Mg, 0.59 mmol) in MeI (3 ml) under an inert atmosphere, in a vial which was then sealed with a Teflon-lined screw-on cap. The reaction mixture was then allowed to stand in the dark at room temperature (outside of the dry box) or at 40°C. The course of the reaction was monitored by TLC, and was judged to be complete in one week at room temperature or 20 hrs. at 40°C. MeI was then removed with the use of a rotary evaporator, and the solid recrystallized from toluene/petroleum ether under an inert atmosphere at -40°C. Pale yellow material, mp. with decomposition and

bubbling 127.5 - 129.5°C, was obtained (363 mg, 95% yield). Calc: C 36.65, H 4.77%, found: C 36.25, H 4.56%.

7a: Synthesis of 7a was attempted in a manner analogous to that used to prepare 4, using $BrCH{=}CH_2$ instead of MeI. Samples were examined by ^{31}P NMR after removal of $BrCH{=}CH_2$, with and without recrystallization. The reaction was also allowed to proceed in one attempt at -40°C for one week, after which the $BrCH{=}CH_2$ was removed at -40°C and the resulting solids examined by IR at ambient temperature. No incorporation of a vinyl group (judging by the absence of any C=C stretch) could be observed.

7b: The attempted syntheses of 7b proceeded in a manner analogous to that used for synthesis of 4.

Decompositions

Melt decompositions were accomplished in sealed tubes under N_2. Solutions for decomposition were prepared under an inert atmosphere in C_6D_6 (0.05 to 0.1 M), in sealed tubes (which were broken before sampling for GC analysis) or in flasks having a straight-bore stopcock capped with a serum cap through which gases and liquids could be sampled via syringe. GC analyses were calibrated with absolute response factors for the gases and/or propane as internal standard. In the solution decompositions, gas and liquid phase were sampled and the total amount of gases formed is reported. In all cases except those in Table IV), gases formed accounted for all the Pt decomposed (± 10%).

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26. While the exact mechanisms of formation of 5 is uncertain, it should be noted that $L_2PtMeCl$ cannot be made directly from L_2PtCl_2; L_2PtMe_2 forms instead. Also, exchange of groups has been noted frequently in Pt(II) and (IV) systems; see for example, R. J. Puddephatt, P. J. Thompson, J. C. S. Dalton, (1977), 1219.

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29. ^{31}P NMR spectra could only be obtained occasionally on a few samples. Consequently, earliest attempts at the syntheses of 7a and 7b were examined by ^{31}P NMR only after removal of excess vinyl halide (so

preliminary ^{1}H NMR could be obtained) and frequently after recrystallization (so that spectra of pure samples would be obtained). Decomposition studies were carried out on several samples prior to ^{31}P NMR, as a means of preliminary characterization.

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CHAPTER III:

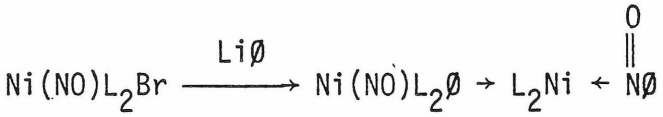
FORMATION OF CARBON-NITROGEN BONDS VIA TRANSITION METAL NITROSYL COMPLEXES

INTRODUCTION

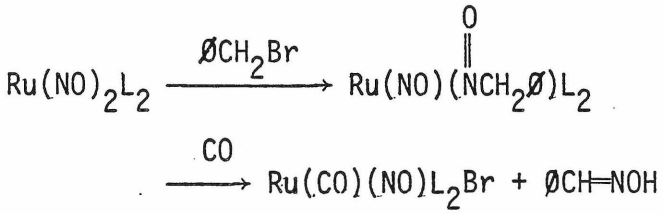
The formation of carbon-carbon bonds at transition metal centers is well established for a variety of systems. In particular, formation of carbon-carbon bonds *via* insertion of CO into a metal-alkyl bond has been observed in many instances (Reaction 1).[1] The presence of two-electron donor ligands frequently promotes the reaction[2]

Reaction 1

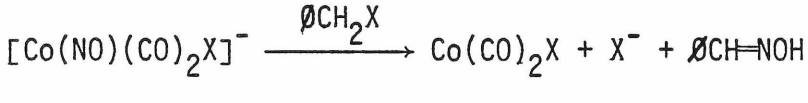
A large number of transition metal nitrosyl compounds are known,[3] including some nitrosyl-alkyl complexes. Several of the complexes apparently form carbon-nitrogen bonds *via* insertion of NO into a metal-alkyl bond in a reaction analogous to the CO insertion shown in Reaction 1. In Reactions 2 and 3, for example, the intermediacy of a metal nitrosyl alkyl compound seems certain. Reaction 4 seems to involve



Reaction 2
Reference 4

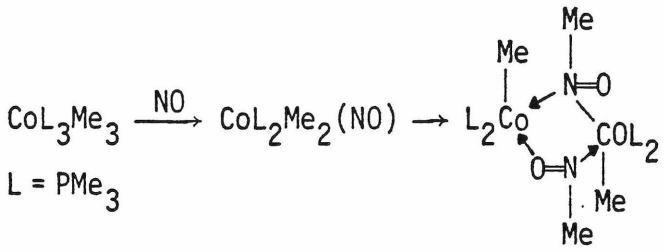


Reaction 3
Reference 5

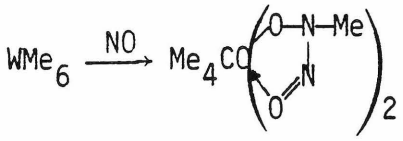


Reaction 4
Reference 6

coordinated $O{=}NCH_2\emptyset$, formed *via* NO insertion. Other cases (Reactions 5 and 6) involve free NO, but it seems that NO is again inserting into metal-carbon bonds, presumably after coordination to the transition metal.

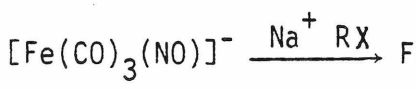


Reaction 5
Reference 7



Reaction 6
Reference 8

A great many transition metal compounds also contain carbonyl ligands, and it is often observed that reactions proceed at the carbonyl ligands with almost total disregard for the nitrosyls. An example is given in Reaction 7, and one should be aware that this is a widespread



Reaction 7
Reference 9

phenomenon.

It seemed to us that the most logical system in which to look for insertion of NO into a metal-carbon bond would be one where both NO and an alkyl group were attached to a transition metal, with no coordinated CO ligands. Such a system has been reported by Legzdins et al. for the Group VI metals: $CpM(NO)_2R$ (M = Cr, Mo, W) (Cp = η^5-cyclopentadienyl).[10] We decided to explore the chemistry of these to see if we could effect insertion of NO into the metal-carbon bond.

RESULTS AND DISCUSSION

The chromium nitrosyl compounds 1 can be prepared from $CpCr(NO)_2Cl$ 2 as described by Legzdins et al.,[10] and $CpCr(NO)_2Cl$ can be prepared from $CrCl_3$ in a procedure reported by Wilkinson[11] (Reaction 8). There is some indication in the literature that the molybdenum and tungsten compounds analogous to 1 and 2 are somewhat less stable than the chromium compounds,[11] and therefore they were not prepared or investigated.[12]

$$CrCl_3 \xrightarrow[2.\ NO]{1.\ Na^+Cp^-} \underset{2}{CpCr(NO)_2Cl} \qquad \text{Reaction 8}$$

$$\xrightarrow{R_3Al} CpCr(NO)_2R$$

1a, R = Me
b, R = n-hexyl
c, R = isobutyl
d, R = Ø

We prepared 2 as described by Wilkinson, but with the use of a large excess of NO bubbled through the reaction solution (instead of the approximately one equivalent used by Wilkinson), with the result that the yield improved somewhat (up to 59% from 30 - 50%). 2 is air stable as a solid and in solution for periods of up to an hour, but apparently decomposes upon storage at 18°C under rigorously air-free conditions over a period of several months. 1 was also prepared as described. It similarly is air stable as a solid or in solution, but decomposes over a period of weeks as a solid, stored carefully (18° C, air free).

Treatment of 1a with Two-electron Donors

In experiments designed to see insertion of NO into the chromium-alkyl bond, 1a was treated with a variety of two-electron donors. These experiments are described below. One should keep in mind the stability of 1a during this discussion: except for the aforementioned sporadic tendency of 1a to decompose upon standing, it is quite stable thermally, remaining unchanged after heating in benzene solution at 100°C for 24 hr. Photochemically, it is considerably less stable: a solution of 1a will be entirely decomposed in less than an hour of irradiation with an unmodified mercury lamp.

Treatment of 1a with CO caused no change in the starting material.

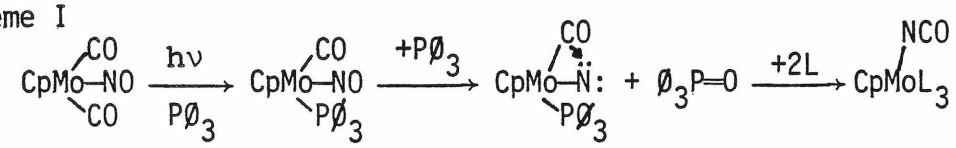
Treatment of 1a with $P\emptyset_3$ resulted in decomposition of 1a at a rate faster than that observed in the absence of $P\emptyset_3$ but with formation of no tractable products. When 1a was irradiated in the presence of $P\emptyset_3$, however, a new organometallic product could be observed by NMR to be growing in. Attempts to drive the reaction to completion only resulted in destruction of both starting material and product, until a modified light source (< 4750 Å) was used. We could then obtain reaction mixtures containing more product than 1a, but long irradiation times would still destroy both materials. The ultraviolet spectrum of 1a exhibits a maximum at 4610 Å, while the spectrum of a mixture of 1a and product shows a shoulder at approximately 5750 Å, the apparent maximum for the product. Evidently, the product is photoreactive, and is destroyed at rates comparable to those of its formation. It was subsequently discovered that other phosphines reacted more quickly and cleanly with 1a.

The thermal reaction of 1a and $PMe_2\emptyset$ was complete in 5 hrs. at ambient temperatures; the new product appeared, on the basis of its NMR spectrum, to be quite similar to the product of the $P\emptyset_3$ reaction. PMe_3 reacted even more rapidly, so that all 1a had reacted within two hours at ambient temperatures. The reaction with PMe_3 was also quite clean (there seemed to be a correlation with the faster reactions being cleaner), and it was decided to concentrate our efforts on this reaction.

Reaction of 1a with PMe_3

Two equivalents of PMe_3 are required to convert all of 1a to product; if only one equivalent is used, half of the 1a is rapidly converted to product and the other half remains unchanged. There are actually two products, one of which is $O{=}PMe_3$, identified by comparison of NMR and IR spectra and melting point to that of an authentic sample. McPhail[13] has reported that $CpMo(CO)_2(NO)$ in the presence of $P\emptyset_3$ is converted upon irradiation to $CpMo(NCO)(CO)L_2$, and speculates that this is accomplished *via* the mechanism shown in Scheme I. A nitrosyl ligand is deoxygenated by the $P\emptyset_3$ to form a nitrido species; the nitride then inserts into a Mo-CO bond. Phosphines are also known to deoxygenate organic nitroso

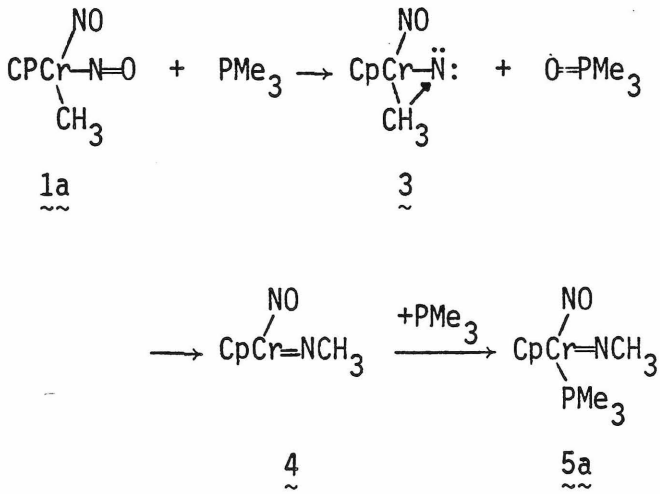
Scheme I



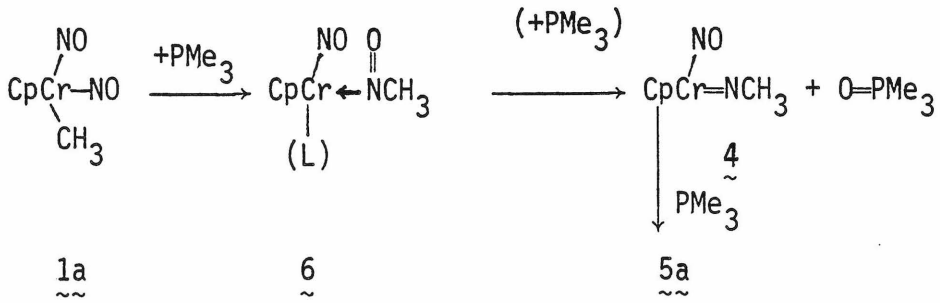
compounds, generating organic nitrenes,[14a] and to deoxygenate nitroso compounds datively bond to transition metals.[14b] This suggests that in our reaction, PMe_3 is deoxygenating a nitrosyl or nitroso species, perhaps

via one of the two mechanisms shown in Schemes II and III.

Scheme II



Scheme III



In Scheme II, deoxygenation of a nitrosyl ligand generates a nitrido species 3, which then inserts into the $Cr-CH_3$ bond. The 16-electron nitrene 4 which is so formed then adds another molecule of PMe_3 to achieve an 18-electron configuration. All of the intermediates in this mechanism are expected to be very reactive, which is consistent with the fact that no intermediates are observed by NMR during the course of the reaction. In a variation on this Scheme, PMe_3 might initially coordinate to 1a and the coordinated phosphine deoxygenate a nitrosyl ligand to

generate nitrido species 3. (This is the variation favored by McPhail[13] for his system.)

In Scheme III, a datively-bound nitroso ligand is formed first, in one or more steps; PMe_3 may or may not be involved in any of the steps required to form 6, and may or may not be coordinated when deoxygenation occurs to form the nitrene 4. One might expect a nitroso species such as 6 (L = PMe_3, so that an 18-electron configuration is achieved) to be stable and observable; for this reason, the mechanism shown in Scheme II is favored. Neither mechanism has been proven, and another mechanism may be operating. However, note that the same product, 5a, is predicted by either of the Schemes.

Isolation and Assignment of Structure of 5a

Isolation of the product of the reaction between 1a and PMe_3 proved to be more difficult than anticipated. After removal of solvent under vacuum from the completed reaction mixture, $O{=}PMe_3$ could be separated from the solid residues by sublimation (room temperature, 0.1 μ) onto a -78°C cold finger.[15] In this way, crude 5a containing only a few percent of $O{=}PMe_3$ and other impurities (visible in the NMR spectrum) was obtained in 80% yield. A variety of techniques were explored to further purify the material.

During attempts to recrystallize 5a, it was discovered that allowing 5a to stand in benzene, THF, acetonitrile or diethyl ether for periods of hours resulting in apparent partial decomposition as evidenced by formation of black, gummy, intractable solids. The problem was less pronounced

with methylene chloride or hydrocarbon solvents, but recrystallization from or precipitation from any combination of these solvents resulted in material which showed only slight enrichment of 5a to impurities.

Chromatography of 5a on Florisil, neutral alumina I, neutral alumina V, neutral alumina I deactivated with PMe_3, or basic alumina V resulted in apparent decomposition. One could obtain mixtures of 5a and a new material by rapid (less than one minute) washing of 5a through basic alumina I or chromatography at -50°C on the same support, but no pure 5a was obtained with any of these efforts. 5a does not sublime.

The structure of 5a was assigned on the basis of its NMR, IR and mass spectra. These are contained in Table I. The NMR spectrum of 5a clearly shows a cyclopentadienyl resonance at δ5.50; a doublet at δ1.21 which, based on its chemical shift and ^{31}P-^{1}H coupling constant can be reliably assigned to a coordinated PMe_3 group; and one other CH_3 group, most probably derived from the methyl group in 1a. The sensitivity of the chemical shift of this group to concentration and solvent is reminiscent of the solvent shifts of NCH_3 in $MeCl_2M(ON(Me)NO)_2$, M=Nb, Ta.[16] The IR spectrum exhibits a strong band at 1630 cm^{-1}, which can be reasonably assigned to a linear nitrosyl ligand (although this is somewhat ambiguous, as both bent and bridging nitrosyls can also display bands in this region).[3b] IR data on many of the known metal nitrenes is unfortunately lacking, but Chatt has assigned bands in the region of 1090 cm^{-1} to a metal-nitrogen stretch in some rhenium nitrenes, and has noted a band at approximately 1315 cm^{-1} which seems to be characteristic of the NMe group in these compounds.[17] The latter band is often obscured by bands due to phosphine ligands in molybdenum nitrenes.[18] The band we have observed at 1040 cm^{-1} may then be assigned to a Cr=N stretch, and

Table I

Spectral Data for 5a

NMR(C_6D_6),δ	1.08 (d, J = 1 Hz, 3H), :N–Me[a]	
	1.21 (d, J = 13 Hz, 9H), PMe_3	
	5.50 (s, 5H), Cp	
IR(C_6D_6), cm^{-1}	1630, 1585 (sh), NO stretch	
	1040 (broad), Cr=N stretch	
MS, m/e (rel. int.)[b]	252(4)	parent ion
	234(1)	
	222(31)	parent ion - NO
	220(28)	
	207(100)	222 - CH_3
	205(74)	
	192(13)	
	186(11)	parent - C_5H_6
	177(19)	
	162(19)	
	117(31)	CpCr

a. This value is very solvent and concentration dependent.

b. Peaks which can be accounted for by chromium isotopes have been omitted for clarity. Some of the peaks which are not assigned may be due to loss of ethylene (from Cp) from various fragments, which has been observed for $CpCr(NO)_2Cl$: J. Muller, F. Ludemann, S. Schmitt, J. Organomet. Chem., I69 (1979), 25.

the NMe band obscured by phosphine bands.

The mass spectrum of the organometallic product shows a peak at m/e 252, which corresponds to the parent ion, and the most abundant fragment at m/e 207 corresponds to a loss of Me and NO. Tentative assignments have been made for most of the major fragments. (A mass spectrum of 5a, when it had been briefly exposed to air, showed a peak at m/e 253 and none at m/e 252, indicating that it perhaps acquired a proton from the air; this is not inconsistent with the stability and chemistry of the compound described below.) The structural assignment is therefore as shown in Scheme II.

Since 5a could be obtained only in 95% purity, elemental analyses, molecular weight determination or an X-ray crystallographic structure have not been performed.

Reactions of 5a

The brief studies described in this section have been performed with approximately 95% pure 5a, obtained as described above.

Heating 5a for four hours at 70°C in benzene solution (0.3 M) resulted in nearly quantitative conversion to one new organometallic product (which has not been identified) and methane. Methane is also instantly obtained upon dissolution of 5a in methanol, or upon treatment of 5a with H^+.

Treatment of 5a with H^- resulted in formation of free PMe_3 as the only isolable product. No reaction of 5a with ethylene occurred, up to temperatures sufficient to decompose 5a.

Other Chromium Nitrenes 5b, 5c and 5d

$CpCr(NO)_2R$, R = n-hexyl, isobutyl, and ϕ (1b, 1c and 1d, respectively) were prepared in a manner analogous to that described for 5a.[10] They were similarly allowed to react with two equivalents of PMe_3, and reactions were followed by NMR.

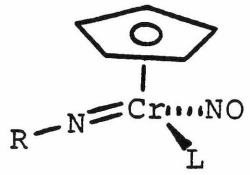
The reaction of $CpCr(NO)_2$(n-hexyl) 1b with PMe_3 proceeds at roughly the same rate as observed for 1a. $O{=}PMe_3$ and the nitrene 5b are formed. This nitrene is apparently more reactive than the methyl nitrene, for it began to disappear even before all of the starting material had reacted. At least six new resonances appeared in the cyclopentadienyl region of the NMR. No attempt was made to isolate these compounds. NMR data for the reaction are listed in Table II.

It was thought that the wide variety of products from 5a was perhaps due to insertion into C–H bonds along the n-hexyl chain. We hoped to simplify the system by changing from an n-hexyl to an isobutyl group.[19] $CpCr(NO)_2$(isobutyl) 1c forms nitrene 5c and $O{=}PMe_3$, but unfortunately this nitrene, too, further reacts to give a mixture which shows at least seven different peaks in the cyclopentadienyl region of the NMR spectrum, at rates comparable to those of the n-hexyl nitrene. NMR data are again listed in Table II.

The reaction between $CpCr(NO)_2\emptyset$ 1d and PMe_3 is complete within 15 minutes; this is at least twenty times faster than when R=Me. The phenyl nitrene does not undergo further reactions. 1d is deoxygenated so readily that we have been able to generate a $P\emptyset_3$-substituted nitrene, $CrCr(NO)(:N\emptyset)(P\emptyset_3)$ 5e. Data for 5d and 5e are included in Table II.

Table II

NMR Data for Chromium Nitrenes 5



Compound	R	L	NMR(C_6D_6),δ
5a	Me	PMe_3	1.08 (d, J = 1 Hz, 3H), R = Me[a] 1.21 (d, J = 13 Hz, 9H), PMe_3 5.50 (s, 5H), Cp
5b	n-hexyl	PMe_3	0.81 (m, 2H), $-CH_2-C_5H_{11}$ 1.3 to 1.8 (m, 20H), $-CH_2-C_5H_{11}$ + PMe_3[b] 5.49 (s, 5H), Cp
5c	isobutyl	PMe_3	1.0 to 1.8 (m, 18H), R = isobutyl + PMe_3[b] 5.47 (s, 5H), Cp
5d	Ø	PMe_3	1.14 (d, J = 12 Hz, 9H), PMe_3 5.68 (s, 5H), Cp 7.2 (m, 5H), R=Ø
5e	Ø	$PØ_3$	5.65 (s, 5H), Cp 7.2 (m, 20H), phenyl groups

a. Very solvent and concentration dependent.

b. Spectrum too poorly resolved to allow a more specific assignment.

Neither of the phenyl nitrenes was found to be significantly more stable than 5a, so that purification was again difficult.

While organometallic nitrenes are relatively novel[21] and deserving of investigation, the difficulty in obtaining pure materials in this system makes it a poor choice for such a study, and further work is not planned.

EXPERIMENTAL

General

THF, diethyl ether, benzene and benzene-d_6 were vacuum transferred from sodium benzophenone ketyl prior to use. Acetonitrile and CH_2Cl_2 were distilled from CaH_2 and degassed (three freeze-pump-thaw cycles) prior to use. Toluene and petroleum ether (35 - 60°C) were stirred over two portions of H_2SO_4, then over two portions of $KMnO_4$ in 10% H_2SO_4, then dried before vacuum transfer from sodium benzophenone ketyl.

Proton NMR spectra were obtained on an EM-390 Varian Associates NMR Spectrometer; IR spectra were obtained on a Perkin-Elmer 257 grating infrared spectrometer. Mass spectra were performed by Jet Propulsion Laboratory, Pasadena, California. Gas chromatographic analyses were performed on a Hewlett-Packard 5750 Research Chromatograph with Porapak Q (9' x 1/8", 80°C) for hydrocarbon gases and a Varian Aerograph 90-P on Penwalt (28% on Chromosorb R 80/100, 5' x 1/4", 50°C) for amines.

Manipulations of air sensitive materials were accomplished in a Vacuum Atmospheres Recirculating Dry Box, on a vacuum line, or under argon using standard Schlenk techniques.

$CpCr(NO)_2Cl$ was prepared according to the method of Wilkinson[11]

except that NO gas was bubbled through the reaction solution, which improved the yield (from 30 - 50% to 59%). The compounds $\underset{\sim}{1}$ were prepared following the procedure described by Legzdins.[10]

Irradiations were performed with an Oriel medium-high pressure Hg lamp; the samples were placed in Pyrex tubes and water-cooled.

Stability of $\underset{\sim\sim}{1a}$

$\underset{\sim\sim}{1a}$ was heated in C_6D_6 (0.5 M) at 100°C in a sealed NMR tube for 24 hrs. All of the $\underset{\sim\sim}{1a}$ remained unchanged.

Irradiation of $\underset{\sim\sim}{1a}$ for 1 hr with an unmodified light source resulted in its complete decomposition. Use of 3900 or 4750 Å filters greatly increased the photochemical stability of $\underset{\sim\sim}{1a}$, which is then largely unchanged after 1 hr of irradiation. $\underset{\sim\sim}{1a}$ absorbs in the visible with a maximum at 4610 Å.

Reactions of $\underset{\sim}{1}$ with Phosphines

Reactions with phosphines were all performed similarly. $\underset{\sim}{1}$ (0.5 M) in C_6D_6 and 5 equivalents of phosphine (either weighed into an NMR tube or measured on a vacuum line) were allowed to react in an NMR tube, and the reaction followed by periodically recording the NMR spectrum. Individual results are described below.

$\underset{\sim\sim}{1a}$ + $P\emptyset_3$

$\underset{\sim\sim}{1a}$ and $P\emptyset_3$ gave no reaction at room temperature and, when heated at 100°C for 24 hrs., resulted only in the destruction of $\underset{\sim\sim}{1a}$ with no

appearance of new products.

When 1a and $P\emptyset_3$ were irradiated with an unmodified light (10 min.), a new product could be observed to grow in (NMR: δ5.53 (s, 5H), Cp; 1.21 (s, 3H), Me) . It was impossible to drive the reaction to completion, however, as both 1a and the product disappeared upon further irradiation (20 min. more).

Use of a 3900 Å filter improved the situation somewhat, but the best results were obtained with a 4750 Å filter. One could then obtain, in 1 hr., a 2-to-1 mixture of 1a to product. Further irradiation caused partial disappearance of both species, and a new peak in the NMR at δ5.47, in small amounts. For the product $CpCr(NO)(:NMe)(P\emptyset_3)$: NMR ($C_6D_6$) δ1.21 (s, 3H, Me), 5.53 (s, 5H, Cp), 7.2 (m, 15H, phenyl); IR(C_6D_6): 1640 cm^{-1} (NO stretch); UV 4610 Å (residual 1a and perhaps also product), 5750 Å (shoulder).

1a + $PMe_2\emptyset$

1a and $PMe_2\emptyset$ reacted completely in 5 hrs. at ambient temperature to give $CpCr(NO)(:NMe)(PMe_2\emptyset)$: NMR($C_6D_6$) δ1.25 (partially obscured by $PMe_2\emptyset$, 3H, Me), 1.30 (d, J = 9Hz, $PMe_2\emptyset$), 5.50 (s, 5H, Cp), 7.2 (m, 5H, phenyl). The reaction was not very clean and the NMR resolution was poor.

1a + CO

No reaction at all was observed between 1a and CO (1 atmosphere) over a period of days.

$\underset{\sim\sim}{1a}$ + PMe_3

$\underset{\sim\sim}{1a}$ reacted completely with PMe_3 in 2 hrs. at ambient temperature. The spectral data for the product are included in Table I.

Preparative scale reactions between $\underset{\sim\sim}{1a}$ and PMe_3 were run in round-bottom flasks, using 0.5 M $\underset{\sim\sim}{1a}$ and 2.2 equivalents of PMe_3. Solvent was removed under vacuum, and the resulting red-brown residues purified by various techniques. $O{=}PMe_3$ was best removed *via* sublimation (0.1 μ, room temperature), occasionally cleaning the cold finger and stirring the solids. This afforded an 80% yield of 95% pure $\underset{\sim\sim}{5a}$.

Recrystallization, precipitation and chromatography were attempted in the dry box using a variety of solvents (benzene, THF, acetonitrile, diethyl ether, CH_2Cl_2 and petroleum ether, either alone or in combination) and solid supports (Florisil, neutral alumina I, neutral alumina V, neutral alumina I deactivated with PMe_3, basic alumina V). None of these efforts produce $\underset{\sim\sim}{5a}$ that was any purer than the material simply obtained after removal of $O{=}PMe_3$. Chromatography at -50°C on basic alumina I under argon was similarly unsuccessful.

$O{=}PMe_3$

Authentic $O{=}PMe_3$ was prepared by treating PMe_3 (0.1 M) with NO gas in methanol solution.[20] NMR (C_6D_6) δ0.97 (d, J = 12.6Hz); IR 1295, 1290, 1195, 1975, 930, 847, 730 cm^{-1}; mp 140 - 141°C. No reaction occurred between PMe_3 and NO in benzene solution.

1b, 1c and 1d with Phosphines

These reactions were run in an entirely analogous manner. Spectral data for the complexes can be found in Table II.

Reactions of 5a

Using 95% pure 5a, a few preliminary studies of its reactivity were made.

The thermal decomposition of 5a was accomplished by heating 5a in benzene C_6D_6 (0.3 M) in a sealed NMR tube at 70°C for 4 hrs. A peak in the NMR spectrum at δ5.19 (IR: 1595 cm^{-1}) was evidently due to a new organometallic product, which, along with methane, was formed in nearly quantitative yield. The new product was not identified.

Dissolution of 5a in CD_3OD (0.3 M) or CD_3OD containing one equivalent of H_2SO_4 resulted in an immediate color change (from red-brown to green) and formation of methane. Addition of more acid or NaOH resulted in no further changes.

Treatment of a solution of 5a in THF-d_8 (0.2 M) with 2.5 equivalents of $LiAlH_4$ at 0°C, followed by warming to room temperature, resulted in a color change to dark brown. After two hours, the reaction mixture was treated with H_2O (50 µl/ml THF), 15% NaOH (50 µl/ml THF) and additional H_2O (200 µl/ml THF). All volatile materials were then vacuum transferred away from the reaction mixture and examined by gas chromatography. Only $P(CH_3)_3$ could be detected.

5a in C_6D_6 (0.3 M) was treated with an equivalent of ethylene in a sealed NMR tube. The reaction was followed by NMR. No reaction occurred

in 10 hours at room temperature; heating the tube resulted in decomposition of 5a identical to that observed in the absence of ethylene.

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15. To achieve good separation, the residues had first to be finely crumbled. During the course of the sublimation, the cold finger had to be cleaned off several times and the solids stirred. The residues could not be heated.

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19. There are only three types of C—H bonds into which insertion could occur in an isobutyl group, versus six in an n-hexyl group. Additionally, insertion is probably not occurring with the C—H bonds in position 1, since the methyl nitrene does not undergo the reaction, so that the isobutyl group presents two C—H bonds versus five in n-hexyl.

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Abstracts of Propositions

Proposition I: Intermediates in the Photochemical Decomposition of Cp_2TiMe_2

$Cp_2Ti{=}CH_2$ has been suggested as an intermediate in the photodecomposition of Cp_2TiMe_2. To confirm this, a cross-over experiment (to rule out intermolecular processes) and trapping of $Cp_2Ti{=}CH_2$ with alkenes, alkynes and/or carbonyl compounds is proposed. It is also suggested that polymerization of alkenes by the photoproducts of Cp_2TiMe_2 be more carefully examined, and methods are suggested for seeing informative intermediates.

Proposition II: New Mixed-Metal Clusters Containing Small Organic Fragments

Instead of treating preformed transition metal clusters with organic molecules, it is proposed that clusters be built by careful addition of a monomeric organometallic species to a dimeric one. In this way, one may be able to achieve clusters containing organic fragments in specific positions. Mixed-metal clusters containing organic fragments are of particular interest, and they are discussed.

Proposition III: A Two-Dimensional Organometallic Polymer

The formation of transition metal polymers containing metal-metal bonds is discussed. It is proposed that the

monomeric metal species be preformed into some particular array before polymerization (formation of metal-metal bonds), and a monolayer, anchored to glass *via* Si-O-Si bonds, is suggested as a means of generating a two-dimensional array.

Proposition IV: Studies of Metallabicyclobutanes

It is proposed that transition metallabicyclobutanes be synthesized by the action of carbenes on metal alkyne complexes (which can also be viewed as metallacyclopropenes). The chemistry of metallabicyclobutanes is discussed; in particular, one might hope to see formation of metallacyclobutenes.

Proposition V: Some Aspects of Organometallic (η^3-allyl) Fluxionality

The endo and exo isomers of $[CpMo(CO)(NO)(\eta^3\text{-}C_3H_5)]^+$ **2** interconvert, but at a much slower rate than that observed for $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ **1**. The latter isomerizes by an apparent rotation about a Mo-allyl bond, without interconversion of the syn and anti protons. NMR and deuterium labelling experiments are proposed, which will determine whether isomerization in **2** occurs *via* a rotation or a π-σ-π mechanism. The deuterium labelled compound will also yield information about the mechanism of formation of **2** from **1** and NO^+.

Proposition I: Intermediates in the Photochemical Decomposition of Cp_2TiMe_2

The photochemical decomposition of a number of titanocene species has been studied by various groups, and in many (although not all) cases parallels the thermal decompositions. The cyclopentadienyl groups can be photolabilized in Cp_2TiCl_2 (Cp = η^5-cyclopentadienyl)[1,2] or $Cp^*_2TiCl_2$ ($Cp^* = \eta^5$-C_5Me_5)[2], and irradiation of these species in chlorinated hydrocarbon solvents results in the formation of $CpTiCl_3$ or Cp^*TiCl_3, respectively (Reaction 1). The radical

$$L_2TiCl_2 \xrightarrow{h\nu} L^{\cdot} + LTiCl_2 \xrightarrow{CHCl_3} LTiCl_3$$

L = Cp or Cp* Reaction 1

species $CpTiCl_2$ and $Cp^{\cdot}$ have been observed by ESR spectroscopy ($Cp^{\cdot}$ as its spin adduct with nitrosodurene).

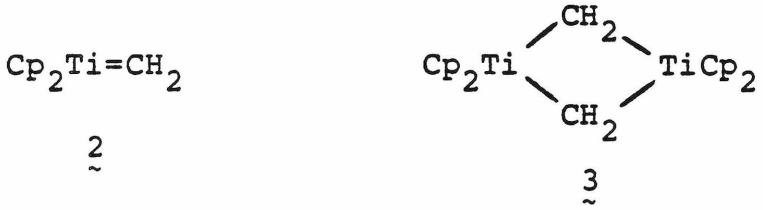
Irradiation of Cp_2TiMe_2 results in the formation of methane and titanocene[3] (Reaction 2). Deuterium labelling studies indicate that other methyl groups and cyclopentadienyl rings serve as sources of hydrogen in the formation of

$$\underset{\underset{\sim}{1}}{Cp_2TiMe_2} \xrightarrow{h\nu} Cp_2TiMe + Me^{\cdot} \rightarrow\rightarrow Cp_2Ti + 2\ MeH$$

Reaction 2

methane; during irradiation in benzene or toluene, no hydrogen is abstracted from solvent. The initial reaction is homol-

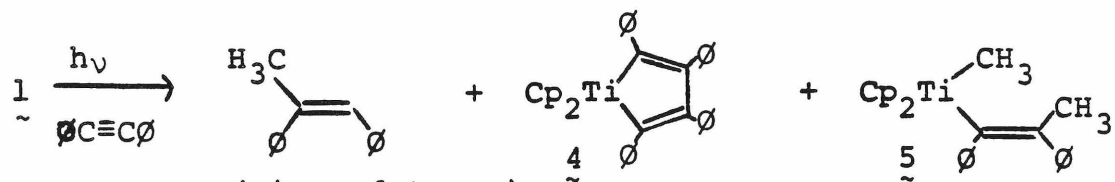
ysis of the Ti-CH_3 bond, and both Cp_2TiMe and Me$^\bullet$ can be observed by ESR (the latter as its spin adduct with 5,5-dimethyl-1-pyrroline-1-oxide).[4] Cp_2TiMe has been observed in the reaction of Cp_2TiCl with MeLi at -78°C, but it is unstable at temperatures above -50°C.[5] The presence of free Me$^\bullet$ (outside of the coordination sphere or titanium or a solvent cage) has been questioned,[6] and this may not be inconsistent with the observed spin adducts, which may be the result of trapping a species other than free Me$^\bullet$. Rausch suggests the possibility of intermediates such as a titanocene carbene 2 or a dimeric species 3, formed from abstraction of hydrogen by Me$^\bullet$ from a methyl group.[3] Homolysis of M-C bonds has been observed in



2 3

other systems, including Cp_2VMe,[7] (bipyridyl)$PtMe_2I$,[8] and $Cp_2Ti(aryl)_2$.[9]

Photolysis of Cp_2TiMe_2 1 in the presence of diphenylacetylene produces methylstilbenes as well as metallacyclopentadiene 4 and titanium methyl alkenyl complex 5 (Reaction 3).[3,10] Note the insertion of a carbon-carbon multiple bond into a metal-carbon bond.



(cis and trans)

Reaction 3

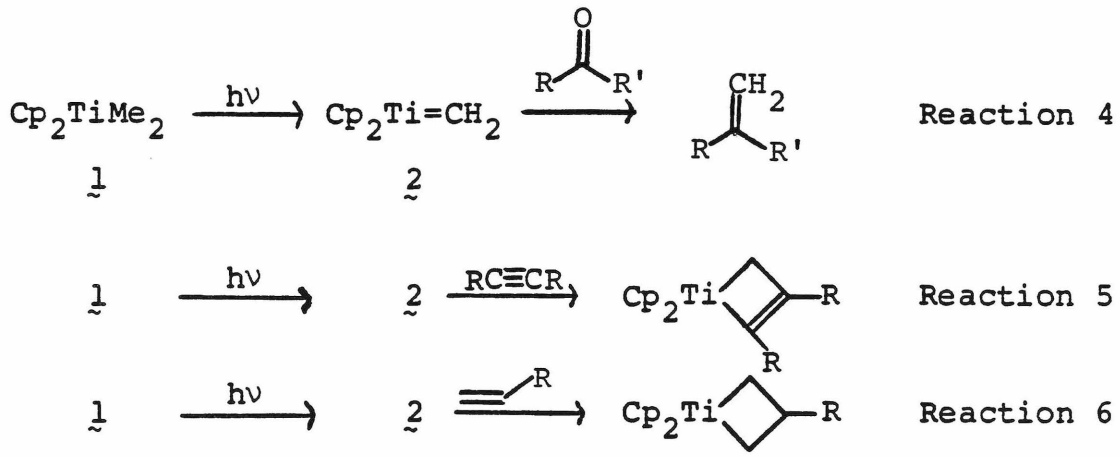
Thermal decomposition of Cp_2TiMe_2 also yields methane, and the source of hydrogen is again both the methyl groups and the cyclopentadienyl rings.[11] Small amounts of ethane are also produced.

It seems likely that there are some common intermediates in the thermal and photochemical decompositions of Cp_2TiMe_2 and the reactions of $Cp_2\overline{TiCH_2Al(Me_2)Cl}$ 6[12] and titanocene metallacyclobutanes.[13,14] Indeed, a titanocene carbene 2 has been postulated as an intermediate in the reactions of titanacyclobutanes with esters[14] and is probably formed when 6 is treated with pyridine.[15] It seems worthwhile, therefore, to propose several experiments to learn more about the mechanism of photochemical decomposition of 1, and to bring together the results of the several lines of research.

Let us first address ourselves to the possibility of a dimeric species such as 3. Since one can obtain two molecules of methane for each molecule of 1 irradiated,[6] a species such as 3 (formed after the loss of one molecule of methane from each of two molecules of 1) must decompose further to give two more molecules of methane. If a dimeric species is formed, or if other intermolecular processes are taking place, it should be possible to detect this in the following cross-over experiment: a mixture of $(\eta^5\text{-}C_5H_5)_2Ti(CH_3)_2$ and $(\eta^5\text{-}C_5D_5)_2Ti(CD_3)_2$ is irradiated. If no methane is formed <u>via</u> an intermolecular mechanism, then only CH_4 and CD_4 will be observed. If a dimeric species such as 3 contributes, or

if some other intermolecular process occurs (such as attack of Cp_2TiMe on 1), one will see CD_3H and CH_3D and perhaps CD_2H_2. The same type of cross-over experiment could be applied to the thermal decomposition of 1 or decomposition of methylene-bridged species 6 with pyridine,[15] and if common intermediates are involved, the same results should be obtained.

If a carbene species 2 is formed, it should be possible to trap it. For example, carbene 2 should react rapidly with a ketone to give the alkene product of methylene for oxygen exchange (Reaction 4);[16] with an acetylene to give a metallacyclobutene (Reaction 5);[12] or with an alkene to give a metallacyclobutane. (Reaction 6).[13] Thus, one could irradiate



Reaction 4

Reaction 5

Reaction 6

1 in the presence of acetone and, if 2 actually is formed from the irradiation of 1, obtain isobutylene. Irradiation of Cp_2TiCl_2 in the presence of acetone gives $Cp_2TiCl_2(OCHMe_2)$, but our system is different: since free Me· is not formed, neither is free Cp_2TiMe (Me· always extracts H before "escape" as CH_4, and leaves behind 2 or $Cp(C_5H_4)TiMe$ or some similar

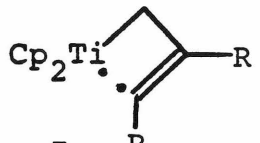
species), and a reaction analogous to that of $CpTiCl_2$ is not necessarily to be expected.

The fact that no titanacyclobutene is observed upon irradiation of 1 in the presence of diphenylacetylene (Reaction 5, R=Ø) does not argue strongly against the intermediacy of 2 in photodecompositions in the absence of diphenylacetylene. The initial excited state formed by the absorption of light by 1 is a Cp→Ti charge transfer state,[2] with increased electron density on titanium; diphenylacetylene is a good electron acceptor.[17] It may be that an exciplex is formed between the excited state 1* and diphenylacetylene ($1^{\cdot+}$ $DPA^{\cdot-}$) and that the products one observes (Reaction 2) reflect the chemistry of this exciplex rather than a generalized reaction of intermediates from photolysis of 1 with alkynes. The experiment should be performed with poorer electron acceptors such as 2-butyne (Reaction 6, R=Me) to give the known[14] metallacyclobutene $Cp_2\overline{TiCH_2C(Me)=C(Me)}$.

Irradiation of 1 in the presence of 3,3-dimethyl-1-butene should afford the metallacyclobutane $Cp_2\overline{TiCH_2CH(t\text{-butyl})CH_2}$ (Reaction 6).[13]

Isolation or detection of titanacyclobutenes or titanacyclobutanes might be complicated by their photoreactivity. Such problems might, however, be avoided by careful irradiation at wavelengths at which 1 absorbs but the metallacycles do not. It is also conceivable that the ability to abstract a hydrogen is much different for $Me^{\cdot}$ (in a solvent cage,

perhaps) and diradicals 7 and 8, which cannot maneuver as easily. Additionally, the two radical centers are perhaps

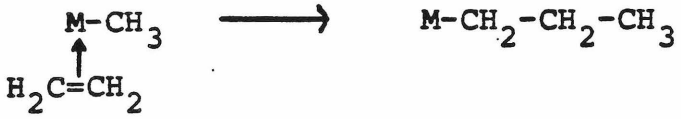


7

8

held in closer proximity in 7 and 8, so that recombination to give ground state metallacycle is more likely. The quantum yield, then, of photoreactions of metallacycles may be much lower than the quantum yield of formation of methane from 1, and this might allow one to build up significant concentrations of metallacycle in photolysis mixtures containing 1 and alkene or alkyne.

Puddephatt has observed that photolysis of 1 in the presence of methyl methacrylate results in polymerization of the alkene, presumably by a free radical mechanism.[6] If, as Rausch suggests,[3] the insertion of diphenylacetylene into the Ti-CH_3 bond is an example of the type of insertion which has been suggested for Ziegler-Natta polymerization catalysts (Reaction 7), then it is perhaps worthwhile to determine which mode or modes of polymerization can occur in this system.

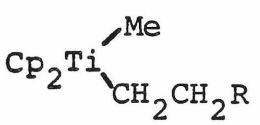


Reaction 7

One should irradiate 1 in the presence of ethylene or propene

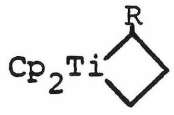
(alkenes typically polymerized with Ziegler-Natta catalysts) and look for insertion products (irradiate 1 in the presence of one equivalent of alkene) or polymers (irradiate 1 in the presence of a large excess of alkene). The insertion products may be quite unstable, but low temperature photolyses are possible. While it is unlikely that the methyl methacrylate polymerization proceeds in an analogous manner, one might want to explore this further, perhaps again looking for insertion products by irradiating 1 in the presence of one equivalent of methyl methacrylate (instead of the excess used by Puddephatt).

Depending on the results obtained above, one might be able to contribute information to the resolution of the controversy over whether Ziegler-Natta polymerization occurs via alkene insertion[18] or metallacyclobutanes.[19] One might, at low temperature, be able to observe (in the irradiation of 1 in the presence of ethylene) either 9 or 10; if the system polymerized ethylene, one might see 11 or 12. One



9, R=CH_3

11, R=$CH_2CH_2CH_3$



10, R=H

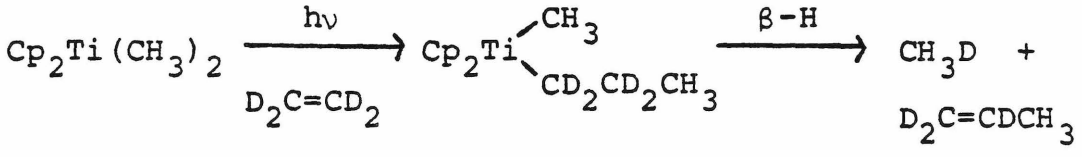
12, R=CH_2CH_3

might not be so lucky, however, but a careful labelling experiment might still yield some information. If intermediates

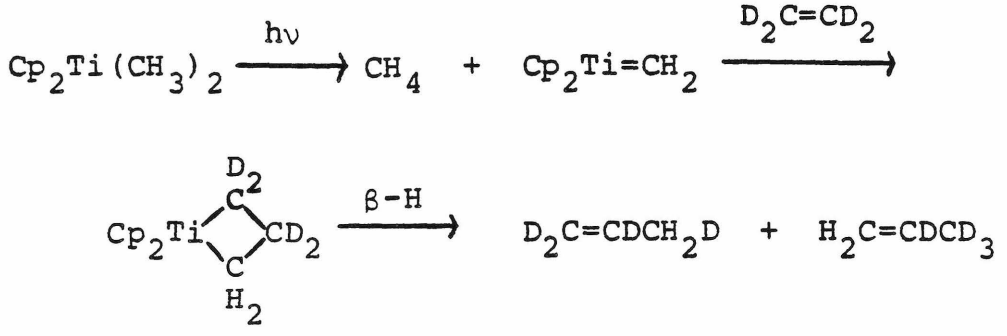
9 or 10 decomposed via β-hydride abstraction, then irradiation of 1 in the presence of ethylene-d_4 would yield hydrocarbon mixtures indicative of the intermediates (Scheme I):

Scheme I

Insertion Mechanism



Metallocyclobutane Mechanism



Other modes of decomposition might similarly yield characteristic mixtures of hydrocarbons.

It seems, then, that a great deal of information is potentially available from the photochemistry of Cp_2TiMe_2, especially as it relates to the chemistry of $Cp_2\overline{TiCH_2Al(Me_2)Cl}$ 6 and polymerization schemes, and further investigation is suggested.

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Proposition II: New Mixed-Metal Clusters Containing Small Organic Fragments

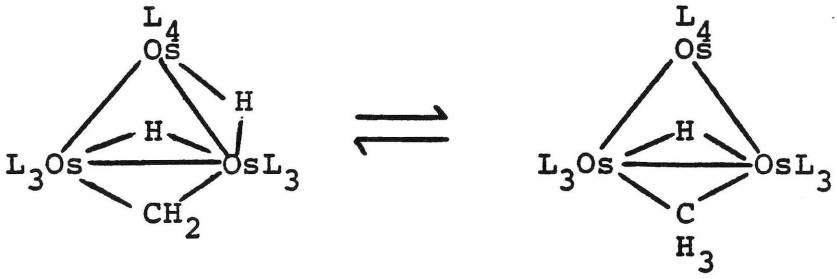
Because of their own potentially interesting chemistry and because they serve as models for understanding catalytic metal surfaces,[1] transition metal cluster compounds have received a great deal of attention.[2,3] Both homometallic and mixed-metal clusters are known, although more work (particularly concerning reactions of clusters with small organic molecules) has been done with homometallic clusters.

The synthetic methods applied to the formation of clusters have relied largely on luck, although rational schemes have been used, mostly consisting of building a cluster by adding one metal at a time (Reaction 1). The reaction conditions used in this approach are frequently not gentle.

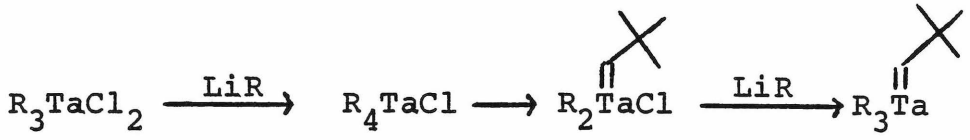
$$M + M \xrightarrow{\text{Step 1}} M{-}M \xrightarrow[M']{\text{Step 2}} \begin{array}{c} M \\ \diagdown\diagup \\ M' \end{array}{-}M \qquad \text{Reaction 1}$$

Interesting work with clusters and small molecules has demonstrated chemistry which has also been observed at single metal centers and on heterogeneous catalytic surfaces. For example, formation of a carbene group from an alkyl group (by α-hydrogen abstraction) has been observed in osmium clusters[4] (Reaction 2) as well as tantalum mononuclear species[5] (Reaction 3). Furthermore, Pettit[6] has suggested that insertion of carbene units (on one metal center or bridging two metal

centers) into metal-hydride bonds gives methyl groups on heterogeneous Fischer-Tropsch catalysts (Reaction 4).

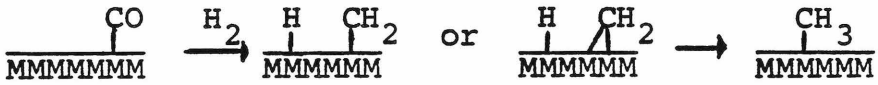


Reaction 2



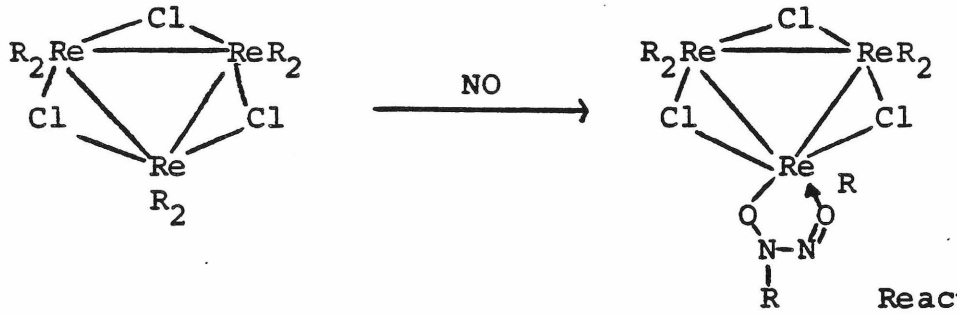
R=neopentyl

Reaction 3

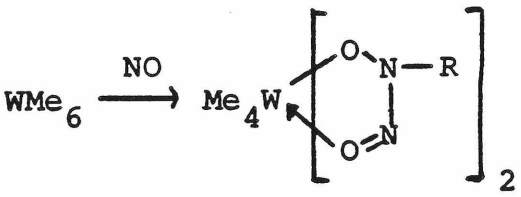


Reaction 4

Other examples of analogous mononuclear and cluster chemistry are shown below (Reaction 5 and 6). Insertion of NO into M-C bonds has been observed for rhenium clusters[7] and mononuclear tungsten.[8]

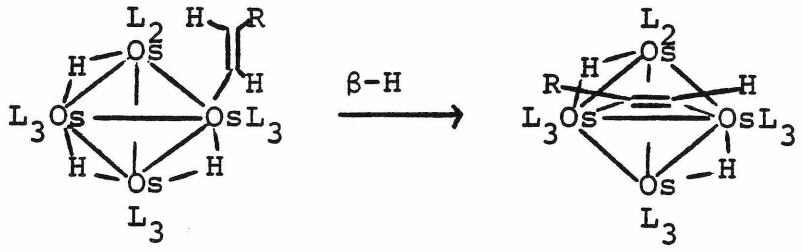


Reaction 5

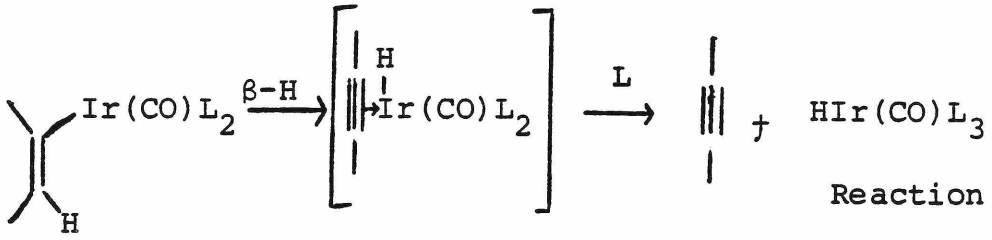


Reaction 6

Abstraction of a β-hydrogen from a vinyl group has been observed in osmium clusters[9] and mononuclear iridium[10] (Reactions 7 and 8).



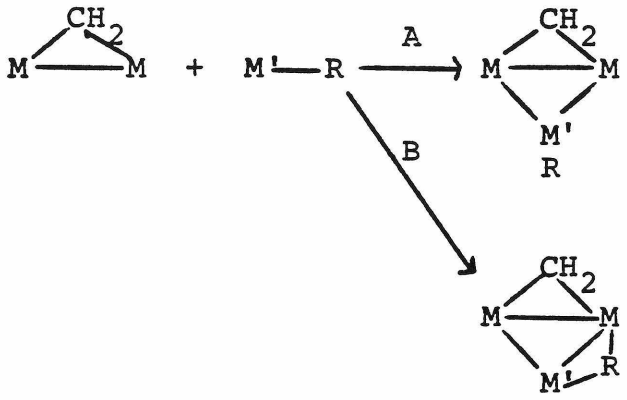
Reaction 7



Reaction 8

The synthesis of cluster compounds containing small organic fragments often consists of allowing a preformed cluster to react with, for example, alkene or N_2CH_2, and taking as the organometallic product whatever Nature chooses to give. Wilkinson has preformed a Re_3Cl_9 cluster and treated it with MeMgX to place methyl groups on the cluster.[11]

It seems that a new synthetic approach, whereby one could more carefully design the organometallic cluster, might be valuable. The approach is similar to that described in Reaction 1: put together mono- or dinuclear organometallic fragments. Either the mono- or dinuclear species involved in Step 2, Reaction 1, might contain a particular organic fragment of interest. For example:



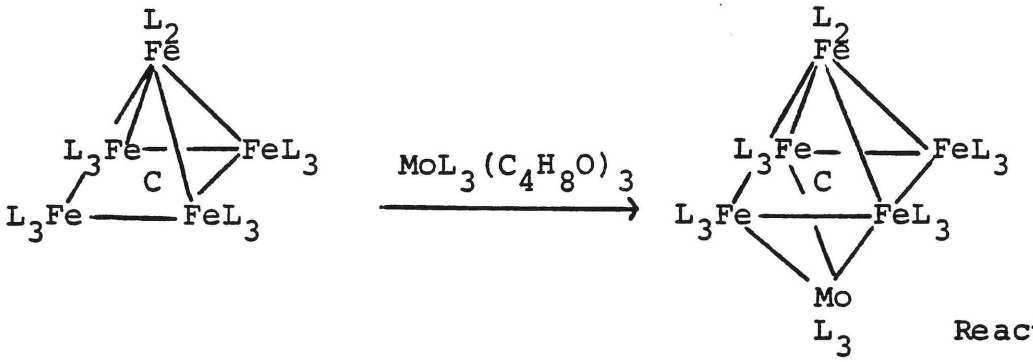
Reaction 9

While particular fragments used to construct the cluster might not retain their integrity (for example, when R=H, a bridging hydride, as shown in Path B, might form), one can probably find systems in which the organic fragments of interest remain (approximately) where one wants them.

To do this successfully, one must employ fairly mild synthetic conditions, so as not to destroy the starting organometallic complexes. Several techniques seem promising: CO ligands can be easily labilized photochemically[12] or with Me_3NO[13a] or (n-butyl)PO,[13b] generating coordinatively unsaturated fragments which can combine to form the clusters; the photochemical approach has been used in some instances.[14] A similar approach has been demonstrated to be general for metal carbide clusters and mononuclear compounds containing readily displacable ligands.[15]

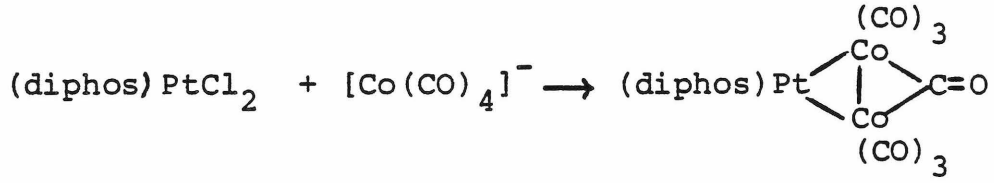
$$Re_2(CO)_{10} + Fe(CO)_5 \xrightarrow[Et_2O]{h\nu} [Re_2Fe(CO)_{12}]^-$$

Reaction 10

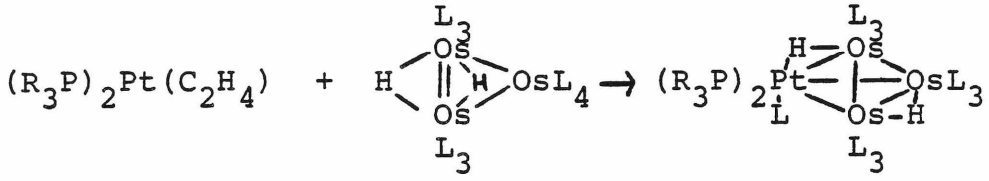


Reaction 11

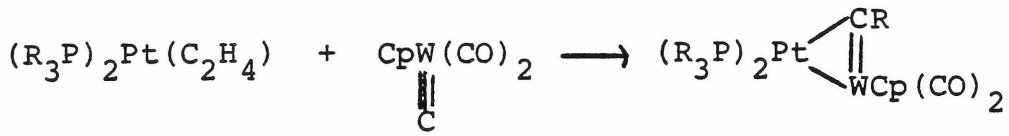
Metal anions can be allowed to react with metal halides (Reaction 12).[16] A coordinatively unsaturated metal species can be allowed to react with another metal (Reactions 13 and 14).[17,18]



Reaction 12



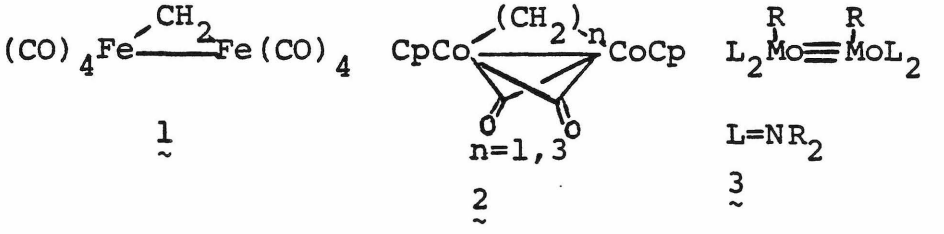
Reaction 13



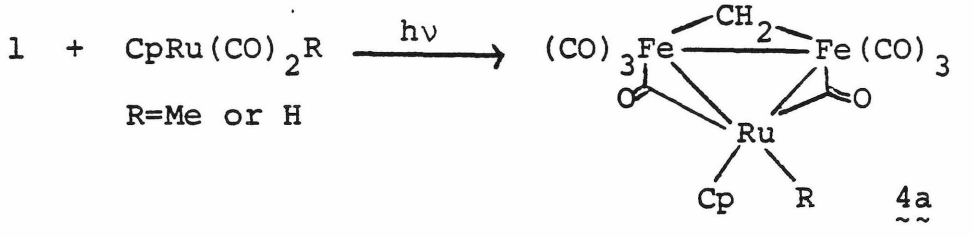
Reaction 14

It is certainly reasonable to suppose that similar methods will succeed with metal complexes containing small organic fragments. A wide variety of mononuclear species are available for consideration; they might contain one or more alkyl or hydride groups, or a metallacycle. A number of interesting

dimeric species are also known, including a diiron methylene 1,[19] dicobalt species 2,[20] and dialkyl dimolybdenum 3.[21] One

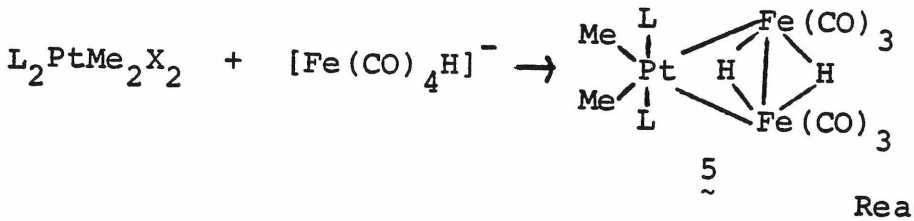


could hope to construct clusters from such fragments. For example, photochemically labilizing CO might lead to the formation of cluster 4a (Reaction 15). (In this and all reactions listed below, the product is a tentative formulation only, and carbonyl, methyl, or other groups may prove to be bridging rather than bonded to one metal, or vice versa.) It may prove to be necessary to choose irradiation wavelengths such that only one starting material is irradiated.



Reaction 15

Metal alkyl halide and a metal anion could lead to compound 5 (Reaction 16). An unsaturated metal-metal bond and an electron-rich metal might lead to cluster 6. (Reaction 17). A synthesis analogous to Reaction 11 ought to yield yet another cluster 7 (Reaction 18).



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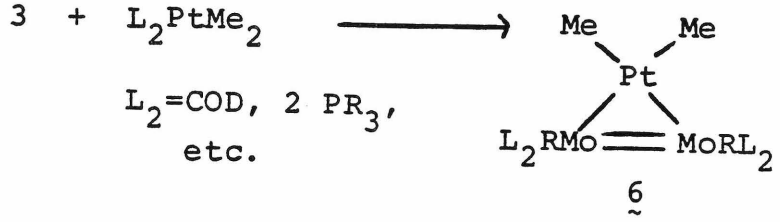
Reaction 16



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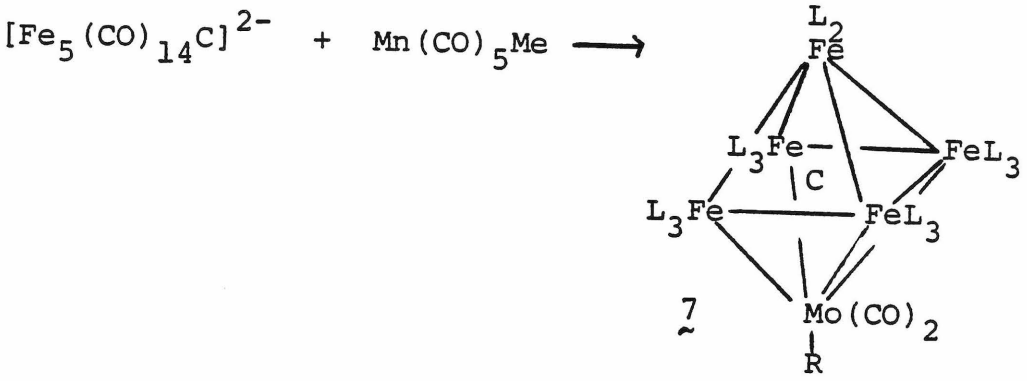
Reaction 17



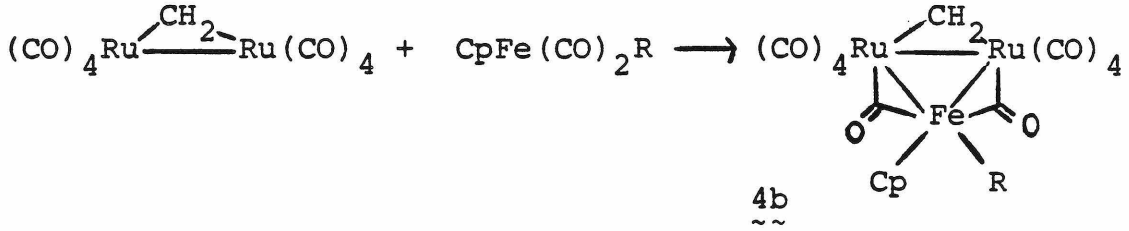
7

Reaction 18

Homometallic or mixed-metal clusters ought to be obtainable via these methods. The examples in Reactions 15-18 show mixed-metal clusters as products.

One would want, of course, to examine the chemistry of the products 4a, 5, 6, and 7. For example, 4a might insert CH_2 into the Ru-R bond to give a $-CH_2R$ group. Reductive elimination from 5 (to give CH_4 or C_2H_6) might occur, or similar processes might be observed with 6 (giving MeR or C_2H_6). Formation of a carbyne (:CR) from R and C might be observed for 7. Of course, one can speculate that a number of other reactions might also occur, but no attempt is made

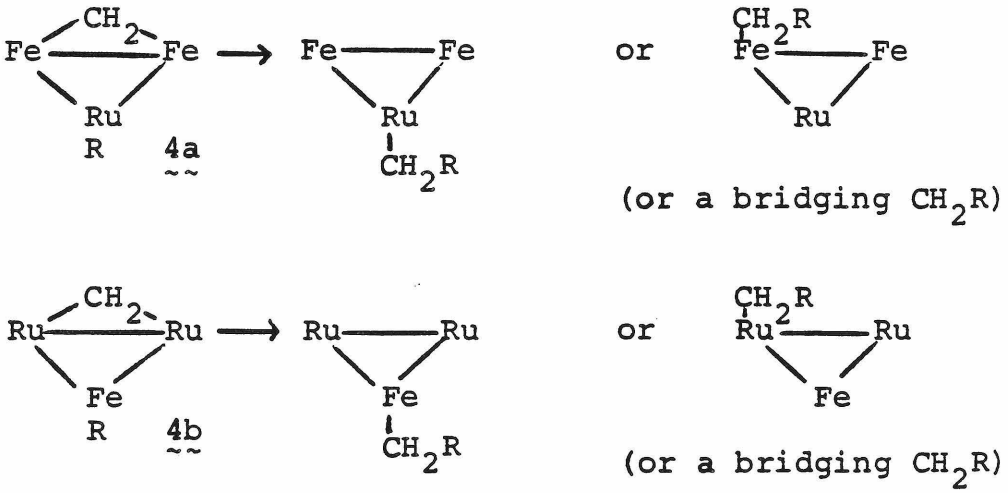
to discuss all of them here. It should be noted, however, that mixed-metal species have the potential to demonstrate a greater variety of reactions than homometallic compounds do. For, example, if one were able to observe insertion of CH_2 into the Ru-R bond in 4a, one might also see an analogous reaction in 4b (the synthesis of which is shown in Reaction 19).[22] In the products, the CH_2R group may be found on the metal atom on which it is formed (which would depend on whether CH_2 inserted or R migrated), or its position may reflect the tendency for the heavier metals to prefer the higher oxidation states (Scheme I).



4b

Reaction 19

Scheme I



It is clearly too early to make specific predictions concerning the results of the experiments suggested here. However, one will certainly be able to obtain new clusters containing intriguing small organic fragments, which should display rich chemistries of their own.

References and Notes

1. A metal cluster is defined as containing three or more metal atoms. Work with bimetallic species provides an important link, and some of it will be referred to.

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5. R. R. Schrock, Accts. Chem. Res., 12 (1979), 98, and references therein.

6. R. Pettit, Division of Inorganic Chemistry, Second Chemical Congress of the North American Continent, Las Vegas, Nevada, August 25-29, 1980.

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17. L. J. Farrugia, J. A. K. Howard, P. Mitrprachachon, J. L. Spencer, F. G. A. Stone, P. Woodward, J. C. S. Chem. Comm., (1978), 260. This method was applied to $H_2Os_3(CO)_{10}$ and $AuMe(P\emptyset_3)$, but $HAuOs_3(CO)_{10}(P\emptyset_3)$ was formed.

18. T. V. A. Ashworth, J. A. K. Howard, F. G. A. Stone, J. C. S. Chem. Comm., (1979), 42.

19. C. E. Sumner, Jr., P. E. Riley, R. E. Davis, R. Pettit, J. Amer. Chem. Soc., 102 (1980), 1753.

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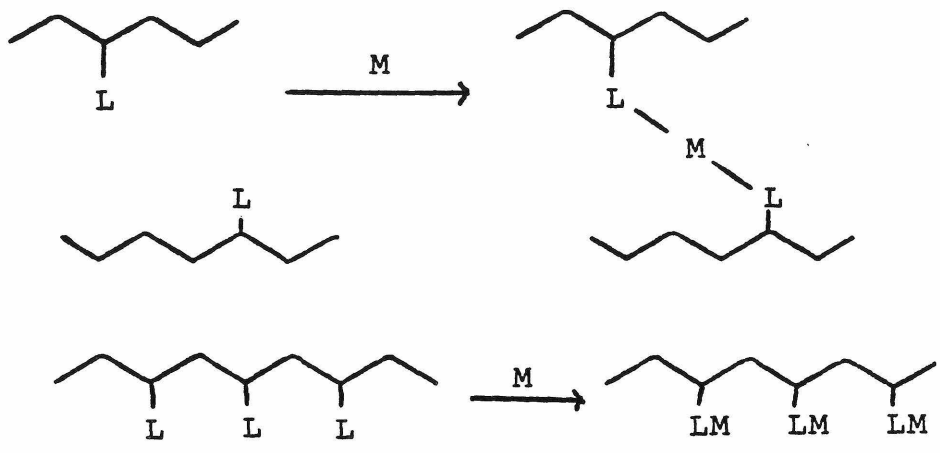
22. $(CO)_4Ru\overset{CH_2}{\frown}Ru(CO)_4$ is not yet known, but it ought to be available by a method analogous to that used to prepare the Fe analog (Reference 19).

Proposition III: A Two-Dimensional Organometallic Polymer

Considering the importance of organic polymers in our lives, it is not surprising that interest has sprung up in organometallic polymers as well.[1] Organometallic polymers may or may not contain formal metal-metal bonds, or be designed for specific through-space metal-metal interactions; they may have organometallic groups incorporated into the polymer chain or pendant from an organic backbone; and a variety of synthetic schemes can be envisioned. However, there are (of course[2]) problems which are rapidly encountered by the experimentalist. Organometallic polymers may display poor solubility, so that purification, handling and characterization are difficult.[3] Clusters[4] or cyclic[5] organometallic species may be obtained instead of linear polymer chains. There are a few examples of linear oligomers containing three transition metals.[5,6]

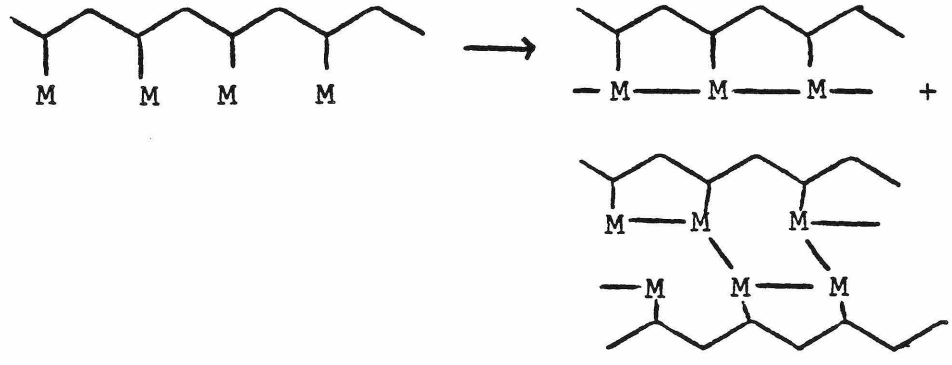
Thus, while the polymerization of a solution of organic monomer is frequently easily accomplished, different techniques may be required for polymerization of organometallic compounds. It is not difficult to think of methods of making organometallic crosslinks (Reaction 1). These are not true organometallic polymers, but organic polymers contaminated with a bit of metal, and one would expect their properties to be very similar to those of other crosslinked organic polymers. It is a simple matter conceptually to extend this idea to a



Reaction 1

Reaction 2

polymer with many pendant organometallic groups, complexed to pendant ligands. Such materials may be quite insoluble, and only a small percentage of the pendant ligands might be substituted before precipitation occurred. Steric or other problems might also lead to a low percentage of substituted



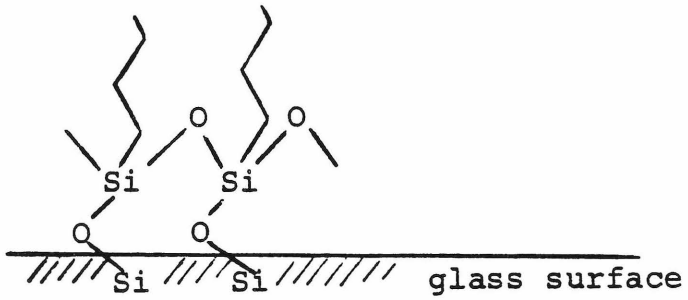
Reaction 3

ligands. Furthermore, if one wished to make metal-metal bonds crosslinking would certainly ensue (Reaction 3).

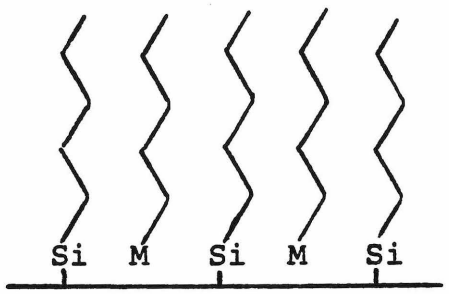
It is proposed to explore a new approach to organometallic polymers containing metal-metal bonds: with some organic polymer or other material, the monomeric metal species are

aligned in some configuration, and then bonds between the monomers are formed. The method might allow one to construct polymers containing metal-metal bonds in an orderly fashion.

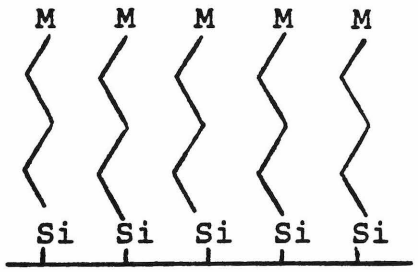
It is difficult to think of a linear (one-dimensional) array which would not present the crosslinking problems described above (Reaction 3), unless the metals could perhaps be sterically constrained to react only with their neighbors on the chain. However, a two-dimensional array might be achieved. Sagiv[7] has described the formation of mixed monolayers on various surfaces. The most stable of the monolayers contained n-octadecyltrichlorosilane (OTS) chemically bonded to a glass surface. Other materials (fatty acids, cyanine dyes) were physically absorbed on the surface, and good



quality monolayers could be achieved with dye constituting up to 50-60 % of the mixed monolayer coverage. Such monolayers supply a method of achieving ordered arrays of organometallic species, depicted below (1 and 2), either by using an organometallic species with a long hydrocarbon tail as one of the components of the monolayer, or by arranging organometallic species at the other end of the hydrocarbon chain attached to a $-SiCl_3$ group.

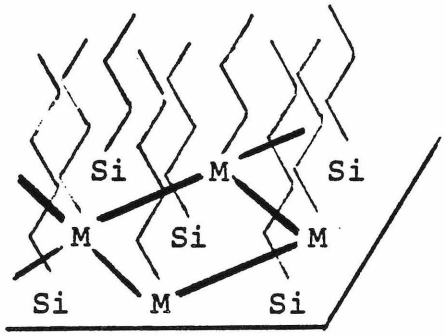


1

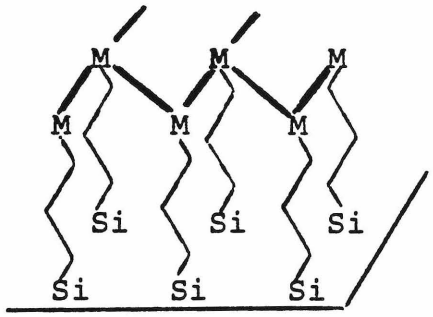


2

Such monolayers might have interesting properties of their own, or they might allow the preparation of two-dimensional polymers from the formation of metal-metal bonds in the array (3 or 4).



3

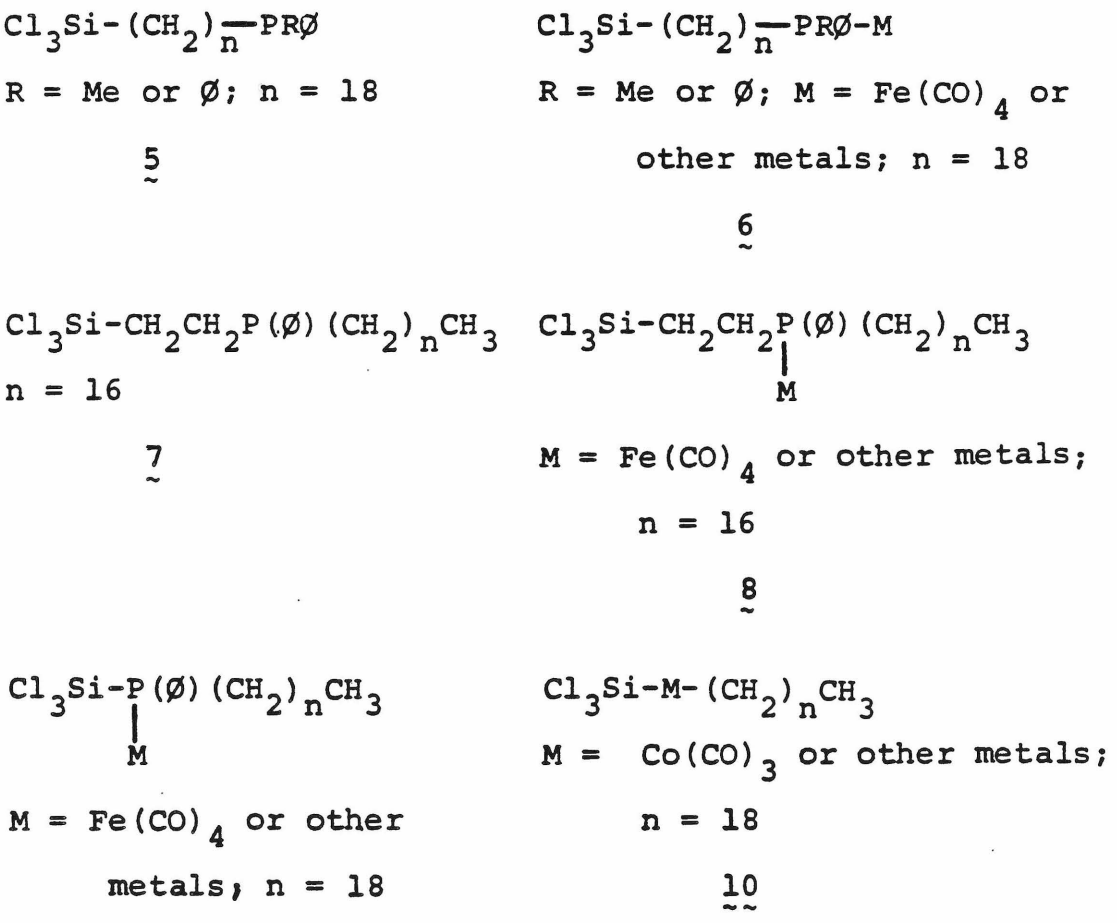


4

To form an array of type 1, one would need to know more about the interaction of the metal species M and the surface (i.e., whether it is chemically bonded or physically absorbed on the surface). Metals which are physically absorbed will quite likely be attached reversibly, just as cyanine dyes and fatty acids are reversibly attached,[7] so that the array will not be as stable. Chemically bonded species would be an improvement, but still be not be as stable as the OTS monolayers, which derive stability from polymeric bonding; the M-O-Si bond might not be as strong as the Si-O-Si bond, either.

Additionally, the choice of metals that form strong M-O bonds is rather limiting, especially if one wants to subsequently polymerize the metals *via* metal-metal bonds.[8] Clearly, further investigation into the (chemical or physical) bonding of metals with long hydrocarbon tails to form monolayers (or to modify surfaces) is warranted, but it will not be discussed further here.

Taking advantage of the chemical bond formed by OTS (or other $RSiCl_3$ species), it is suggested that the following materials be formed into monolayers:



Compound 5[9,10] ought to give a monolayer with phosphine groups at the upper[11] surface. The choice of the group R may be governed by steric effects (two phenyl groups at the upper surface may be too bulky to allow the formation of a good monolayer). A transition metal complex can be attached after the monolayer is formed. $M(CO)_5$ (M=Fe, Ru, Os), or $[Mn(CO)_5]_2$ (M=Mn, Re) are good choices for the metal, since they are known to form metal-metal bonds (in clusters) readily; they even form linear triatomic species.[4] Other metals might, of course, be used. Monomeric or dimeric metals might be acceptable, although dimeric species might be too bulky to complex to all of the (closely packed) phosphine groups. One could make a mixed monolayer, consisting of 5 and OTS, to achieve a suitable spacing of phosphine groups at the upper surface. Alternatively, one could complex the metal to the phosphine before forming the monolayer (Compound 6).

The long hydrocarbon chains holding the transition metal complex in a "fixed" array may be too flexible. Compounds 7[12] and 8 would largely solve this problem, as they will hold the metal complex rigidly near the glass surface. Compounds 9[13] and 10[14] would also hold the metal rigidly; however, their ability to form stable monolayers will partly depend on the stability of the Si-P and Si-M bonds.[13]

A monolayer formed from these species might be interesting in its own right. Even more fascinating, though, is the polymer that will be formed as photolysis or treatment

with ($\underline{n}$-butyl)$_3$PO or Me$_3$NO gently removes CO and promotes the formation of metal-metal bonds.[15] With the metal species constrained to be co-planar (or nearly so) by the long hydrocarbon chains (and attachment near the glass surface for $\underset{\sim}{7}$, $\underset{\sim}{8}$, $\underset{\sim}{9}$ and $\underset{\sim\sim}{10}$), planar polymers might form. An investigation of the properties (physical, chemical, catalytic, electrical) of these, while beyond the scope of the present proposal, would certainly be interesting.

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2. Murphy's Law.

3. G. D. Goretsas, R. H. Grubbs, unpublished results.

4. Many reviews are available which discuss the formation of clusters from monomeric organometallic species. One of the most recent is: W. L. Gladfelter, G. L. Geoffroy, Adv. Organomet. Chem., 18 (1980), 207. There are many references therein to earlier reviews.

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9. Compound 5 can be easily prepared using the standard methods for synthesis of $RSiCl_3$ and $RP\emptyset_2$ (Reference 10a).

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11. As the monolayer is depicted in 1, 2, 3, and 4, the bottom of the monolayer is attached to the glass surface, and the upper "surface" is that formed by the ends of the hydrocarbon tails.

12. $\emptyset_2PCH_2CH_2SiCl_3$ is known (Reference 10a and patents cited therein), as are a number of analogous compounds.

13. $Fe(CO)_4P(SiMe_3)_3$ is known: H. Schumann, O. Stelzer, J. Organomet. Chem., 13 (1968), C52, although it is uncertain whether Cl_3SiPR_2 will be a good ligand. Si-P bonds

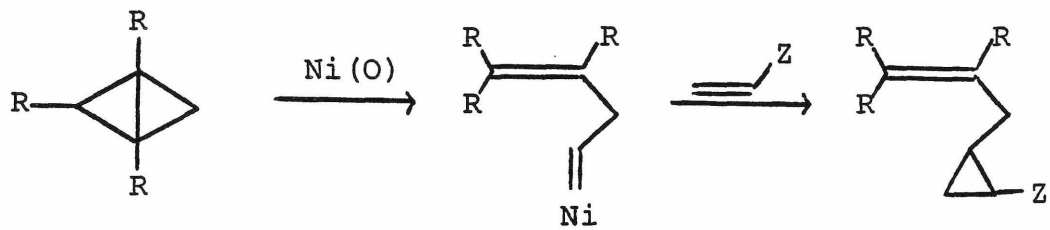
are susceptible to hydrolysis, so that water on the glass surface might cleave this bond before hydrolyzing the Si-Cl bonds (Reference 10b).

14. $CpFe(CO)_2SiMe_3$ and other transition metal-Si bonded species are known, although I am not aware of any metal-$SiCl_3$ species (Reference 10c).

15. (a) M. Wrighton, Chem. Rev., 74 (1974), 401. (b) D. J. Darensbourg, N. Walker, M. Y. Darensbourg, J. Amer. Chem. Soc., 102 (1980), 1213. (c) Y. Shvo, E. Hazum, J. C. S. Chem. Comm., (1975), 829.

Proposition IV: Studies of Metallabicyclobutanes

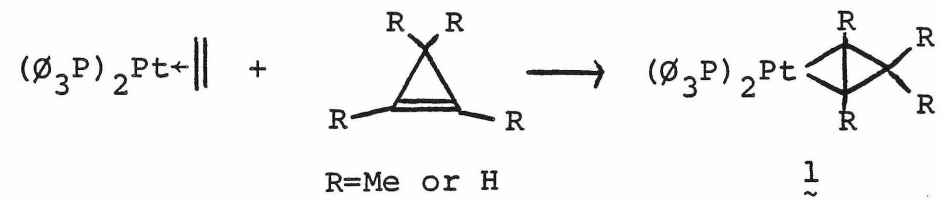
Bicyclo[1.1.0]butane isomerizes at temperatures above 150°C to butadiene,[1,2] and concerted[3] and diradical[4] mechanisms have been proposed for the rearrangement. In the presence of nickel(0) catalysts, bicyclobutanes undergo an intramolecular retro-carbene reaction[5] to apparently give a nickel carbene, which is trapped by electron-poor olefins (Reaction 1). Silver cation opens bicyclobutanes rapidly at



Reaction 1

moderate temperatures; and reactions of other strained ring molecules with metals have been studied.[1]

One example of a transition metallabicyclobutane is known: the reaction of platinum(0) and cyclopropene yields 1 (Reaction 2).[6] The compound has considerable σ-character

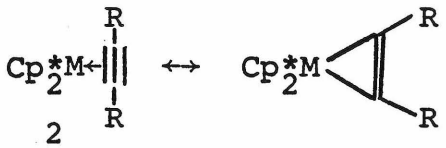


1

Reaction 2

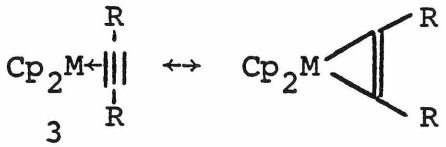
in the Pt-C bonds.[7] Compound 1 releases cyclopropene when treated with carbon disulfide.[6]

A number of other transition metal alkyne complexes, which may be viewed as cyclopropenes, are known.



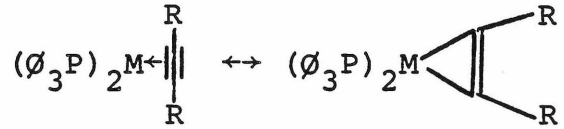
2

Cp*=(η^5-C_5Me_5)
M=Ti, R=Ø or Me
M=Zr, R=Ø (Reference 8)



3

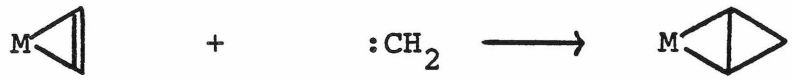
Cp=(η^5-C_5H_5)
M=Mo, R=Ø or Me (References 9,10)
M=W, R=Me (Reference 9)



4

M=Ni, R=Ø (Reference 11)
M=Pt, R=Ø, Me or H (References 11,12)

The addition of carbenes to carbon-carbon multiple bonds is well known,[13] and it is proposed that the transition metal alkyne complexes 2, 3 and 4 be treated with N_2CH_2 to see if metallabicyclobutanes can be obtained in this manner (Reaction 3).



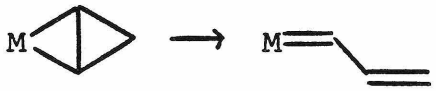
Reaction 3

It seems logical to start with $(Ø_3P)_2Pt(C_2H_2)$, since the resulting metallabicyclobutane is known, but it will be interesting to extend the method to other transition metal systems. It should be noted that the approach used to

synthesize 1 (displacement of ethylene by cyclopropene) appears not to be general.[14]

It will then be interesting to explore the chemistry of the compounds obtained via these reactions. Some of the anticipated products are discussed below.

In an analogous reaction to the isomerization of bicyclobutanes or oxybicyclobutanes[15] one might see formation of a vinyl metal carbene (Reaction 4).



Reaction 4

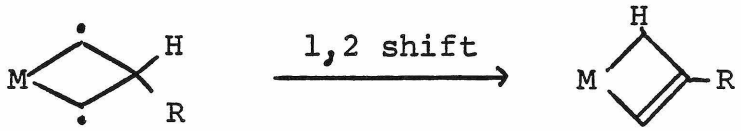
β-hydrogen abstraction might be observed, leading to (η^3-C_3R_3), a ligand which has been observed before, although not via this route.

Reaction 5

Metallacyclobutenes may be formed via a diene intermediate (Reaction 6), a diradical intermediate (Reaction 7), or an η^3-C_3R_3 intermediate (Reaction 8), or via a concerted mechanism (Reaction 9). Some of these routes will be distinguishable from others by appropriate variation of groups on the metallabicyclobutane. It will be especially interesting to examine the reactions of $Cp^*_2Ti(C_2R_2)$, since titanacyclo-

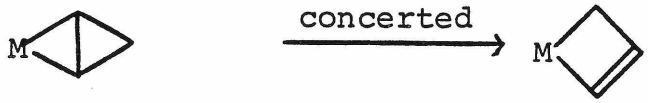
butenes are well known.[17,18]

Reaction 6



Reaction 7

Reaction 8



Reaction 9

While it is too early to predict the reactions of the metallabicyclobutanes formed from reaction of carbene on transition metal alkyne complexes, they will undoubtedly be interesting, and syntheses via this route should certainly be attempted.

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3. G. L. Closs, P. E. Pfeffer, J. Amer. Chem. Soc., 90 (1968), 2452.

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5. R. Noyori, H. Kawauchi, H. Takaya, Tetrahedron Lett., 19 (1974), 1749.

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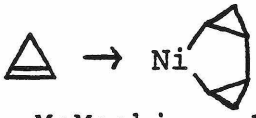
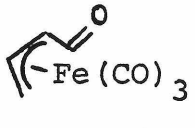
13. T. L. Gilchrist, C. W. Rees, Carbenes, Nitrenes, and Arynes, Appleton-Century-Crofts, New York (1969).

14. The following reactions have been observed:

(a) Ni(O) +  →

M. J. Doyle, J. McMeeking, P. Binger, J. C. S. Chem. Comm., (1976), 376.

(b) $Fe_2(CO)_9$ +  → 

G. Dettlaf, U. Behrens, E. Weiss, Chem. Ber., 111 (1978), 3019.

(c) The same reaction as in (b), with $Fe_2(CO)_9$ and $CpMn(CO)_2(THF)$.
P. Binger, B. Cetinkaya, C. Krueger, J. Organomet. Chem., 159 (1978), 63.

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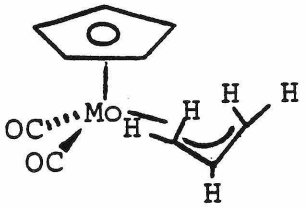
16. One η^3-cyclopropenyl is known, in $CpNi(\eta^3-C_3H_3)$: W. K. Olander, T. L. Brown, J. Amer. Chem. Soc., 94 (1972), 2139.

17. Titanocene metallacyclobutenes are known: F. N. Tebbe, G. Parshall, D. W. Ovenall, J. Amer. Chem. Soc., 101 (1979), 5074.

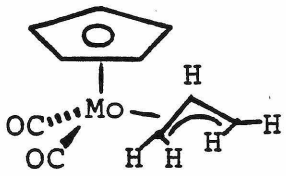
18. K. A. Brown-Wensley, Ph. D. Thesis (Chapter I).

Proposition V: Some Aspects of Organometallic (η^3-allyl) Fluxionality

The molecule $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ ($Cp = \eta^5\text{-}C_5H_5$) can exist in two isomeric forms, 1a and 1b, which interconvert rapidly at room temperature.[1] The isomerization occurs without exchange



1a
endo

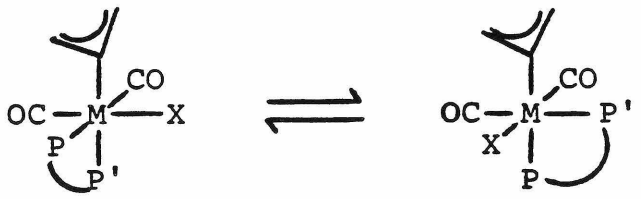


1b
exo

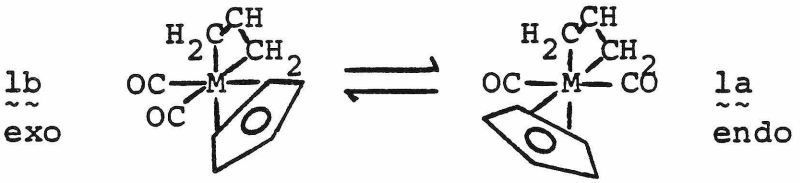
of syn and anti hydrogens, thus ruling out a π-σ-π mechanism, and appears (from the simplest, though not the only viewpoint) to be a rotation about an axis between the metal and the center of gravity of the η^3-allyl. This motion best describes the fluxionality in several other η^3-allylic systems, while the π-σ-π isomerization is well established for others.[2]

Fluxionality in $(\eta^3\text{-}C_3H_5)Mo(CO)_2(diphos)Cl$ can be explained by the rotation wherein the $(\eta^3\text{-}C_5H_5)$-CO-CO system remains fixed with respect to the metal and with respect to each other.[3] This is the simplest explanation for the ^1H, ^{13}C, and ^{31}P NMR spectra observed from -100 to 30°C, although a simultaneous metal-allyl rotation is not excluded by the data (Reaction 1). A similar motion can explain the 1a⇌1b isomeri-

zation, if the molecule is viewed as pseudo-octahedral, with the (η^3-C_3H_5) occupying two positions. Note that, to explain the observed equivalence of the protons on C-1 and C-3, one must not draw a distinction between axial and equatorial positions in the schematic representation (Reaction 2).

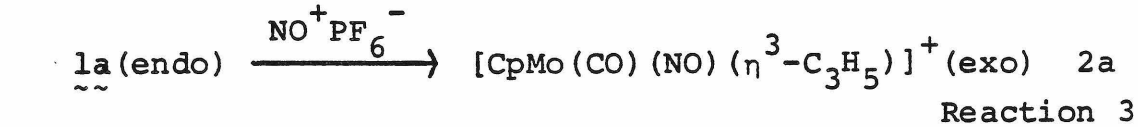


Reaction 1

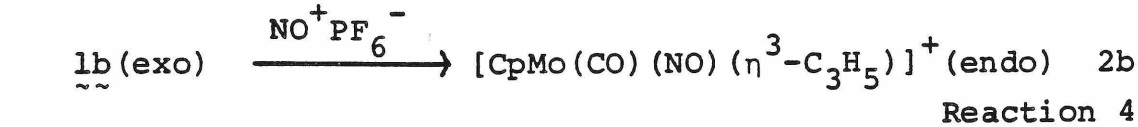


Reaction 2

Interestingly, treatment of 1a and 1b with $NO^+PF_6^-$ results in the following transformations:[4]



Reaction 3

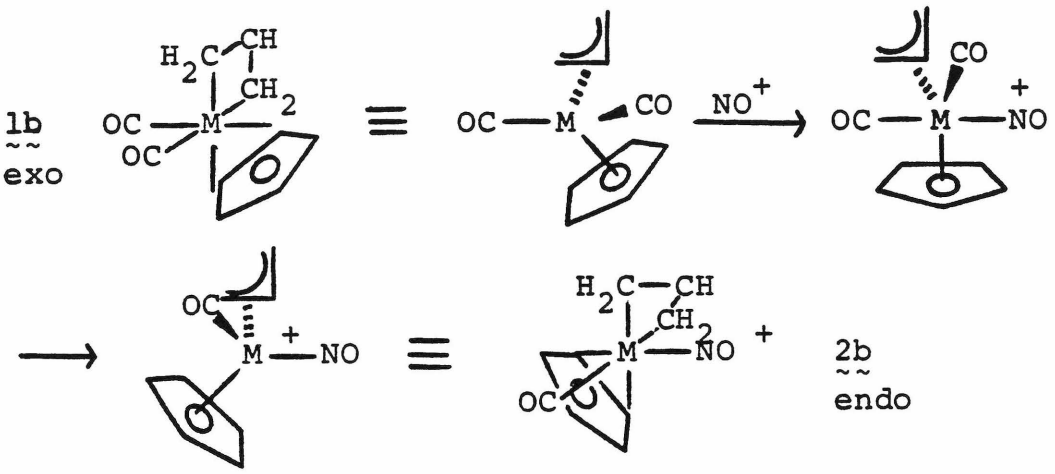


Reaction 4

An S_E2 mechanism, explaining these transformations, is shown in Scheme I.[5] This explanation raises several interesting points.

Faller observes that the products 2a and 2b interconvert

Scheme I



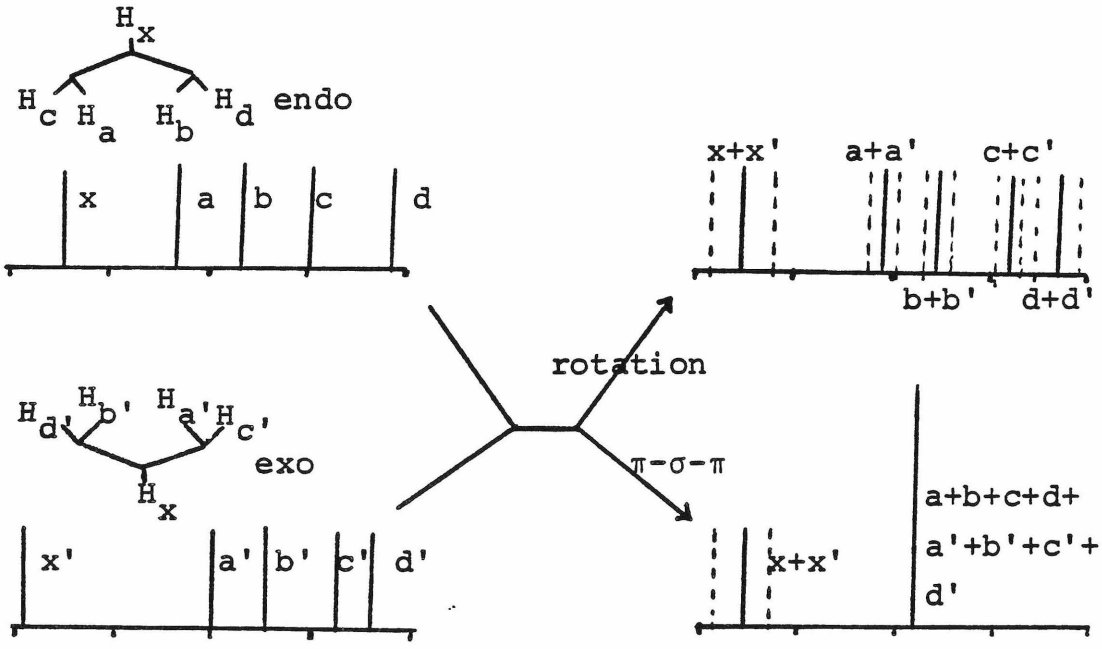
at a rate 10^6 times slower than that observed for the endo-exo isomerization of 1a and 1b.[4] Rotation of alkenes bonded to metals is in general faster for cationic species, due to decreased back-bonding contributions from a less electron-rich metal. Metal nitrosyl compounds, however, tend to rotate olefins less easily, and an explanation may lie in a strong preference for NO to be in some particular geometry (eg. trans) relative to some particular ligand. Faller's observation and this possible explanation lead one to wonder what fluxionality (or lack thereof) might be observed in other η^3-allylic systems where NO^+ has replaced CO (a facile reaction). Systems containing ligands such as $(\eta^2\text{-RN=CR})$[6] or $(\eta^3\text{-RN-N=NR})$[7] might be suitable, although such studies are not the intent of the present proposition.

One wonders what mechanism explains the slow endo-exo isomerization of 2a⇌2b. A similar, but much slower, rotation about the metal-$(\eta^3\text{-}C_3H_5)$ axis is possible, but so is a π-σ-π

interconversion. One can distinguish between these possibilities by examining whether a syn-anti interconversion occurs during the endo-exo transformation. This can be accomplished in two ways.

First, one can examine the high temperature coalescence of the proton NMR signals of 2a and 2b. One will observe coalescence of the ABCDX spectrum of 2a and the A'B'C'D' ' spectrum of 2b into one ABCDX or one A_4X spectrum as one approaches fast enough rates of isomerization, implying, respectively, a metal-(η^3-C_3H_5) rotation or a π-σ-π conversion. This observation will only be possible at high temperatures (which may not be accessible).[8]

Figure 1

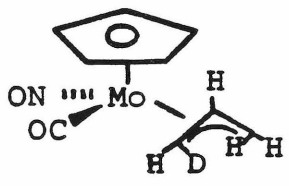


An alternative approach is the spin-saturation technique.

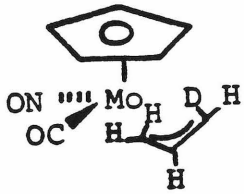
Nuclei in a particular site are saturated, and, provided they move to a new site at a rate comparable to relaxation times (but too slowly to observe coalescence of the signals of the new and original sites), some saturation of the signal of the new site will be observed. Thus one can saturate the H_a signal in 2a, for example, and observe some saturation in either the H_a, or in the $H_{a'}$, H_b, H_c, and H_d, signals in 2b, implying either rotation or π-σ-π interconversions, respectively.

One should note that it has not been established whether or not syn-anti interconversion occurs in 2a or 2b without endo-exo isomerization. Such a question can also be answered by the spin-saturation technique: saturation of H_a in 2a, for example, will lead to partial saturation of H_b, H_c and H_d if π-σ-π conversion occurs without endo-exo isomerization.

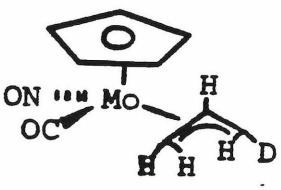
The deuterium-labelled molecules 3a and 3b or 4a and 4b can answer the same sorts of questions, as well as another which will be discussed momentarily. The deuterium will allow one to follow the fate of a particular nucleus without resorting to spin-saturation techniques, but entirely analogous observations will be made. An advantage is that one need not worry about attaining proper temperatures and rates of isomerization, as one will always be able to see the position of the deuterium.



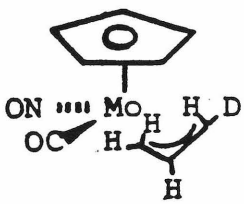
3a (exo)



3b (endo)

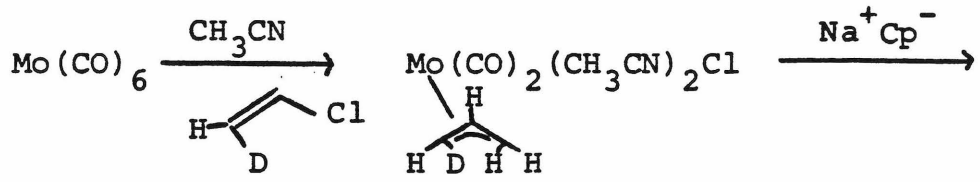


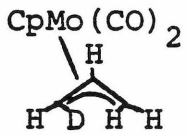
4a (exo)



4b (endo)

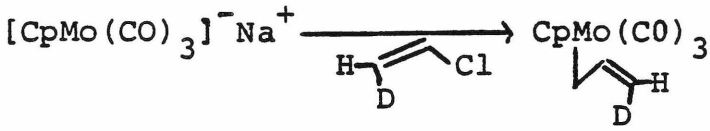
The synthesis of $CpMo(CO)_2(\eta^3\text{-}C_3H_4D)$ 5 can be accomplished easily. Using Z-3-chloropropene-d_1[9] there are two routes:





5a(endo)
5b(exo)

Reaction 5
Reference 10



Reaction 6
Reference 11

The first route (Reaction 5) gives better yields, but may not work if syn-anti scrambling via a $\pi\text{-}\sigma\text{-}\pi$ route occurs in the intermediate $Mo(CO)_2(CH_3CN)_2(\eta^3\text{-}C_3H_4D)Cl$. No such fluxionality is reported for these compounds.[12] The second route (Reaction 6) should avoid this potential problem. One will probably obtain a mixture of endo and exo isomers, which may be separable, or it may be necessary to use a 2-methylallyl derivative, where the exo/endo ratio is higher.

Treatment of 5a with NO^+ will certainly give 3a or 4a or both, and this brings us to an important question: what is the transition state in the proposed S_E2 mechanism, and, in particular, is the allyl π- or σ-bonded? The reaction still needs to be checked kinetically, to be sure it is first order in

each of the reactants (consistent with an S_E2 mechanism). Assuming this to be the case, one can ask whether the transition state is a twenty electron species (as drawn previously to explain the endo-exo conversion upon treatment with NO^+, with a π-bonded allyl) or an eighteen electron species (with a σ-bonded allyl). One might expect an eighteen electron transition state, in which case 5a will, via a σ-bonded allyl (which can rotate), give a mixture of 3a and 4a.

One could also obtain an eighteen electron transition state in two other ways. First, it is well documented[14] that nitrosyl ligands can function as either one or three electron donors. In this case, the nitrosyl ligand enters as NO^+ (NO^+ is usually used to describe a three electron nitrosyl ligand, and NO^- to describe a one electron donor) and is a three electron donor in the product, so it seems unreasonable to envision a one electron NO in the transition state. Alternatively, one can argue that since NO must be donating electrons to the metal as CO leaves, it is unlikely that NO would simultaneously be "backing off" to a one electron donor. The second possibility is that the cyclopentadienyl ring is η^3 instead of η^5, a mechanism for achieving an eighteen electron configuration which has been observed in $(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)Mo(NO)Me$, for example.[15]

It seems reasonable that one may observe products 3a and 4a, implying a σ-bound allyl in the transition state. Alternatively, one might argue for a twenty electron transition

state or an η^3-cyclopentadienyl group, a reaction which is too fast to allow rotation (or is constrained in some other way to prevent rotation), or another mechanism.

In the event that one does obtain either 3a or 4a (but not the mixture, which would be difficult to separate), one can then complement the spin-saturation study described previously, to determine whether syn-anti scrambling accompanies the endo-exo isomerization (or occurs, perhaps, at a faster rate, although still a slow one on the NMR time scale). In any case, the experiments described should allow one to determine (1) whether endo-exo isomerization occurs in 2a⇌2b via the same rotational motion as in 1a⇌1b or via a π-σ-π mechanism, and (2) whether the transition state for the S_E2 conversion of 1a⇌2a or 1b⇌2b contains a σ- or π-allyl.

References and Notes

1. J. W. Faller, C. Chen, M. J. Mattina, A. Jukubowski, J. Organomet. Chem., 52 (1973), 361.

2. J. W. Faller, Adv. Organomet. Chem., 16 (1977), 221, and references therein.

3. J. W. Faller, D. A. Hartko, R. D. Adams, D. F. Chodosh, J. Amer. Chem. Soc., 99 (1977), 1654.

4. J. W. Faller, A. M. Rosan, J. Amer. Chem. Soc., 98 (1976), 3388.

5. It is easiest to see the endo and exo forms in a pseudo-octahedral arrangement, but it is easiest to see concerted substitution of CO by NO^+ from the opposite side in a tetrahedral arrangement. Both representations are shown.

6. R. D. Adams, D. F. Chodosh, Inorg. Chem., 17 (1978), 41.

7. E. Pfeiffer, J. Kuyper, K. Vrieze, J. Organomet. Chem., 105 (1976), 371.

8. Sharp signals as the result of coalescence for 1a and 1b occur at 65°C. Since 2a and 2b isomerize on the order of one million times more slowly, one would need a temperature of perhaps 300°C to see a comparable spectrum, and decomposition of the compounds might occur previous to the attainment of this temperature. A typical NMR spectrometer cannot achieve these temperatures, either. One might, however, see informative spectra at lower temperatures, if not nicely resolved coalesced spectra.

9. The synthesis of Z-3-bromopropene-d_1 has been described: J. A. Katznellenbogen, A. L. Crumrine, J. Amer. Chem. Soc., 98 (1976), 4931. An entirely analogous scheme ought to lead to the chloride.

10. R. G. Hayter, J. Organomet. Chem., 13 (1968), P1.

11. M. L. H. Green, A. N. Stear, J. Organomet. Chem., 1 (1964), 230.

12. H. D. Murdoch, R. Henzi, J. Organomet. Chem., 5 (1966), 553.

13. No distinction is made between a transition state and a highly reactive intermediate in this discussion, and the proposed study would not distinguish between the two.

14. See, for example, R. Eisenburg, C. D. Meyer, Accts. Chem. Res., 8 (1975), 26.

15. F. A. Cotton, G. A. Rusholme, J. Amer. Chem. Soc., 94 (1972), 402.